Porphyrinoids

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Singly and Doubly 1,2-Phenylene-Inserted Porphyrin Arch-Tape Dimers: Synthesis and Highly Contorted Structures

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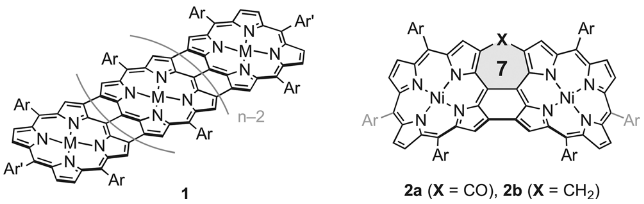
Abstract: *Singly and doubly 1,2-phenylene-inserted Ni^{II} porphyrin arch-tape dimers **3** and **9** were synthesized from the corresponding β-to-β 1,2-phenylene-bridged Ni^{II} porphyrin dimers **5** and **11** via Ni^{0}-mediated reductive cyclization and DDQ/$Sc(OTf)_3$-promoted oxidative cyclization as key steps, respectively. Owing to the fused eight-membered ring(s), **3** showed a more contorted structure than those of previously reported arch-tape dimers **2a** and **2b** possessing a fused seven-membered ring. Furthermore, **9** displayed much larger molecular contortion. As the molecular contortion increases, the Q band of the absorption spectrum becomes more red-shifted and the electrochemcial HOMO–LUMO gap becomes smaller, reaching at 1294 nm and 0.77 eV in **9**, respectively. The effect of molecular contortion on the electronic properties was studied by means of DFT calculations.*

Since the first discovery in 2001, *meso–meso* β–β β–β triply linked porphyrin arrays **1**, namely porphyrin tapes, have attracted considerable attentions owing to the intriguing properties such as extremely narrow HOMO–LUMO gaps, large two-photon absorption cross-sections, high single-molecular conductance, and multi-charge storage capabilities (Scheme 1).[1] In the porphyrin tapes **1**, the component porphyrin segments are connected by direct triple linkages, giving rise to highly planar structures with full conjugation. In contrast, we recently succeeded in the development of an arch-shaped molecular contortion by inserting carbonyl group(s) or methylene group(s) between one of the β–β linkages of porphyrin tapes.[2] Importantly, the resulting porphyrin arch-tapes such as **2a** and **2b** preserved effective π-conjugation over the whole molecule, as evidenced by the small optical and electrochemical HOMO–LUMO gaps, despite the contorted structures. Furthermore, they displayed characteristic properties such as improved solubilities, effective C_{60}-binding behaviors, and arch-to-arch inversion dynamics, which have been scarcely seen for porphyrin tapes **1**.



Scheme 1. Structures of porphyrin tapes **1** and porphyrin arch-tape dimers **2a,b**.

From the structural point of view, the origin of the arch-shaped contortion of **2** can be attributed to the embedded seven-membered ring that causes a structural strain. Such a strategy to incorporate seven-membered ring(s) has been actively employed by a number of researchers.[3] Naturally, incorporation of an eight-membered ring is expected to give rise to larger molecular contortion but such examples have been rather limited, which is probably due to synthetic difficulty arising from large strains. Indeed, it had required a period of two decades to accomplish the synthesis of [8]circulene since the first synthesis of [7]circulene in 1983.[3a,4] To date, benzannulated [8]circulene derivatives[5] and others[6] have been reported.

It is widely known that Ni^{II}-porphyrins are structurally flexible and can take non-planar structures such as ruffled and saddle-like conformations.[7] Actually, the Ni^{II}-porphyrin units of arch-tapes including **2a** and **2b** take highly ruffled conformations to disperse the structural strain caused by the embedded seven-membered ring(s). As a next and more challenging attempt, we envisioned the incorporation of an eight-membered ring into the porphyrin tape skeleton.

As the first target molecule, we designed a singly 1,2-phenylene-inserted porphyrin arch-tape dimer **3**. The synthesis of **3** is depicted in Scheme 2. Initially, β-to-β 1,2-phenylene-bridged porphyrin dimer **5** was synthesized by Suzuki–Miyaura cross-coupling reaction of 2-iodoporphyrin **4**[8] with 1,2-phenylenediboronic acid bis(pinacol) ester. Then, we examined the synthetic procedure used for the synthesis of carbonyl-inserted arch-tape dimer **2a**.[2] Namely, **5** was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and $Sc(OTf)_3$. However, this oxidation unexpectedly produced rearranged product **6** in 59% yield. The X-ray diffraction analysis has revealed that **6** has a skeleton of *meso-β meso-β* doubly linked porphyrin dimer with an additional 1,2-phenylene unit connecting the 3- and 18′-positions (Supporting Information, Figure S65). The structure of **6** indicates that the oxidation of **5** induced 1,2-migration of the phenylene bridge to the neighboring β-position. Although the reaction mechanism remained unclear, *meso–meso* bond formation would be avoided to prevent the formation of a more strained eight-membered ring and instead a less strained six-membered ring was formed, which might trigger the observed rearrangement (Supporting Information, Scheme S1).

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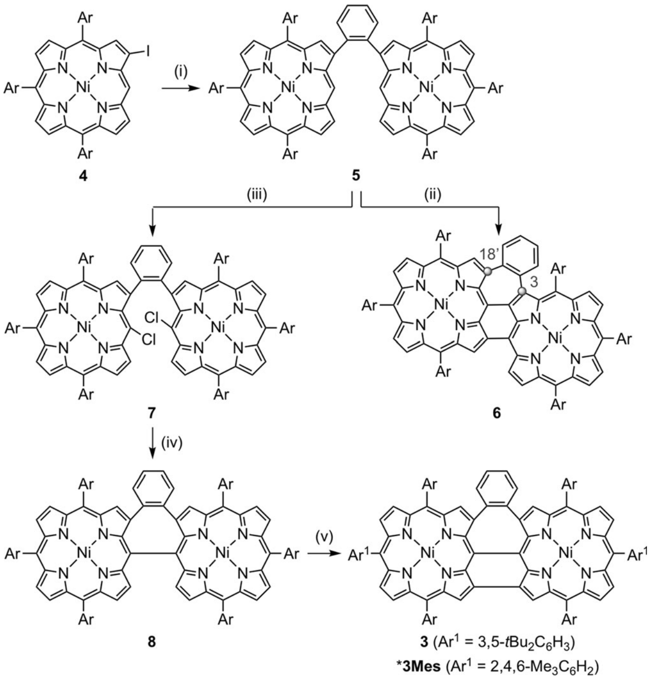
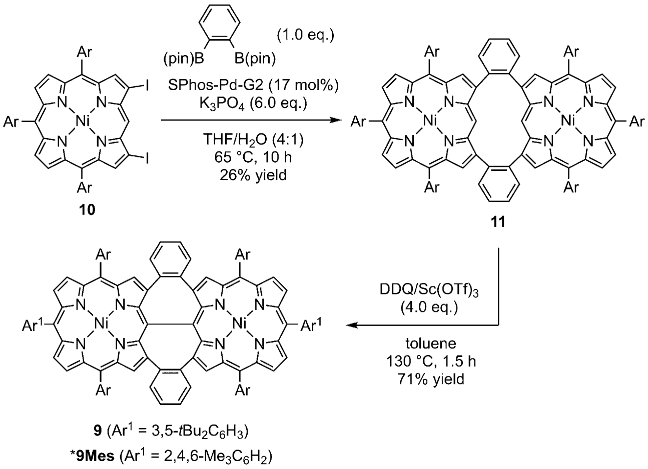


Scheme 2. Synthesis of singly 1,2-phenylene-inserted arch-tape dimer **3**. Reaction conditions: i) 1,2-phenylenediboronic acid bis(pinacol) ester, chloro(2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (SPhos-Pd-G2), K_3PO_4, THF/H_2O, 65 °C, 9 h, 87%; ii) DDQ, $Sc(OTf)_3$, toluene, 60 °C, 1 h, 59%; iii) Palau′Chlor, $CHCl_3$, RT, 6 h, 59%; iv) $Ni(cod)_2$, 1,5-cyclooctadiene, DMF, 100 °C, 9 h, 64%; v) DDQ, $Sc(OTf)_3$, toluene, 80 °C, 2 h, 49%. Ar = 3,5-di-*tert*-butylphenyl.

These results indicate that oxidative *meso–meso* coupling is unsuitable to install an embedded eight-membered ring. Thus, we examined a reductive coupling approach as an alternative route. Treatment of **5** with 2-chloro-1,3-bis(methoxycarbonyl)guanidine (Palau′Chlor)[9] led to *meso*-selective chlorination to afford **7** in 59% yield.[10] The subsequent reductive coupling[11] of **7** with $Ni(cod)_2$ proceeded efficiently to give *meso–meso* directly linked β-to-β 1,2-phenylene-bridged porphyrin dimer **8** in 64% yield. Finally, oxidation of **8** with DDQ and $Sc(OTf)_3$ furnished the desired 1,2-phenylene-inserted arch-tape dimer **3** in 49% yield.

The structure of **3** has been revealed by X-ray diffraction analysis (Figure 1). In analogy with the arch-tape dimers **2a** and **2b**, **3** exhibits an arch-shaped molecular shape. In the crystal structure, the two porphyrin units are crystallographically equivalent, taking a ruffled conformation with a mean plane deviation (MPD)[12] of 0.406 Å. The dihedral angle between the two porphyrin units is 113°, which is smaller than those of **2a** (131°) and **2b** (124°) (Supporting Information, Figure S67). Moreover, the inserted 1,2-phenylene unit is almost perpendicular to the fused diporphyrin segment with a dihedral angle of 84°. These structural features of **3** suggest increased structural strain due to the embedded eight-membered ring as compared with those of **2a** and **2b**.

As an extension, we designed doubly 1,2-phenylene-inserted arch-tape dimer **9**. The synthesis of **9** is shown in Scheme 3. The Suzuki–Miyaura cross-coupling reaction of 2,18-diiodo Ni^{II} porphyrin **10** with 1,2-phenylenediboronic acid bis(pinacol) ester under the Pd/SPhos catalysis furnished β-to-β doubly 1,2-phenylene-bridged Ni^{II} porphyrin dimer **11** in 26% yield. The intermediate **11** was subjected to oxidation with DDQ and $Sc(OTf)_3$ at high temperature of 130 °C. In this case, formation of rearranged products was not observed and the desired doubly 1,2-phenylene-inserted arch-tape dimer **9** was obtained in 71% yield.



Scheme 3. Synthesis of doubly 1,2-phenylene-inserted arch-tape dimer **9**. Ar = 3,5-di-*tert*-butylphenyl.

The structure of **9** was unambiguously determined by X-ray diffraction analysis (Figure 2). Owing to the large structural strain caused by the two incorporated eight-

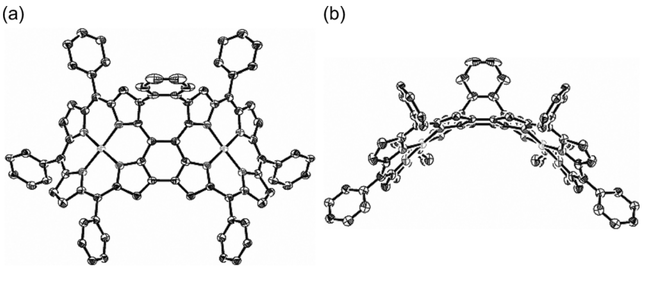


Figure 1. X-Ray crystal structure of **3**.[18] a) Top and b) side views. Ellipsoids are drawn at the 50% probability level. Solvent molecules, *tert*-butyl groups, and all hydrogen atoms are omitted for clarity.

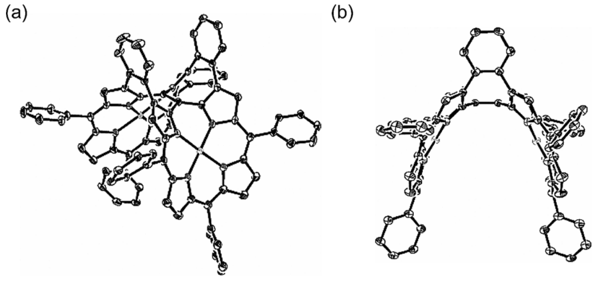


Figure 2. X-Ray crystal structure of **9**.[18] a) Diagonal and b) side views. Ellipsoids are drawn at the 50% probability level. Solvent molecules, *tert*-butyl groups, and all hydrogen atoms are omitted for clarity.

membered rings, **9** displays an extremely contorted structure. The large structural curvature can be outlined by a small dihedral angle of 55° between the two porphyrin units. The MPDs of the two porphyrin units were calculated to be 0.372 and 0.391 Å, indicating that the degree of curvature of the component porphyrin units is comparable to that of **3**. Furthermore, the inserted 1,2-phenylene units are almost perpendicular to the fused diporphyrin segment. Therefore, the conjugative interaction through the 1,2-phenylene units seems to be negligible.

The UV/Vis/NIR absorption spectra of **2a**, **2b**, **3**, **6**, **9**, and **12** are shown in Figure 3. The rearranged product **6** displays split Soret bands at 425 and 512 nm, and a red-shifted Q band at 740 nm. The observed spectral features are quite similar to those of a *meso*-β *meso*-β doubly linked porphyrin dimer,[1c] suggesting negligible electronic perturbation by the inserted 1,2-phenylene unit. The small conjugative interaction through the phenylene unit has been supported by the theoretical calculations (Supporting Information, Figure S78). Singly 1,2-phenylene-inserted arch-tape dimer **3** exhibits split Soret bands at 412, 535, and 566 nm, and a largely red-shifted Q band at 927 nm. The optical HOMO–LUMO gap of **3** is apparently smaller than those of methylene-inserted arch-tape dimer **2b** and porphyrin tape dimer **12**, and comparable to that of carbonyl-inserted arch-tape dimer **2a**. Interestingly, doubly 1,2-phenylene-inserted arch-tape dimer **9** displays a more red-shifted absorption spectrum, with a Q band at 1249 nm. It is worth noting that the intensity of a low-energy Soret band decreases as the molecular contortion increases, which may be attributed to decreased transition dipole moment along the longer molecular axis.

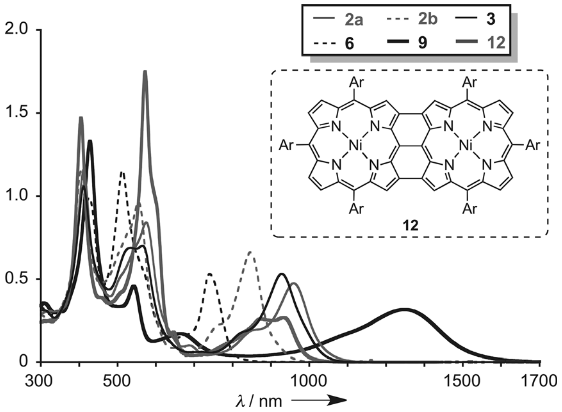


Figure 3. UV/Vis/NIR absorption spectra of **2a**, **2b**, **3**, **6**, **9**, and **12** in CH_2Cl_2. λ = wavelength, ε = extinction coefficient, Ar = 3,5-di-*tert*-butylphenyl.

The electrochemical properties of **3**, **5**–**9**, and **11** were examined by cyclic voltammetry and differential pulse voltammetry (Supporting Information, Figures S68–S74). The selected redox potentials are listed in the Supporting Information, Table S2 along with those of **2a**, **2b**, and **12**. The rearranged product **6** displayed three reversible oxidation waves at 0.28, 0.62, and 0.93 V, and two slightly irreversible reduction waves at −1.35 and −1.60 V. The electrochemical HOMO–LUMO gap (ΔE) was calculated to be 1.63 eV. Singly 1,2-phenylene-inserted arch-tape dimer **3** exhibited three reversible oxidation waves at 0.10, 0.42, and 0.99 V, and two reversible reduction waves at −1.06 and −1.29 V. The ΔE value of **3** (1.16 eV) was smaller than those of **2b** (1.31 eV) and **12** (1.34 eV), and comparable to that of **2a** (1.20 eV). Doubly 1,2-phenylene-inserted arch-tape dimer **9** exhibited four reversible oxidation waves at −0.16, 0.18, 0.99, and 1.12 V, and two reversible reduction waves at −0.93 and −1.11 V. Importantly, the first oxidation potential was negatively shifted from that of **3** by 0.26 V while the first reduction potential was positively shifted by 0.13 V, giving rise to a remarkably small ΔE value of 0.77 eV. These results are in accord with the optical HOMO–LUMO gaps.

Density functional theory (DFT) calculations were conducted at the B3LYP/6-31G(d) (for C,H,N) + LANL2DZ (for Ni) level using the *Gaussian 16* software package (Figure 4; Supporting Information, Figure S75).[13] In line with the experimental results, the HOMO–LUMO gap of **3** (1.63 eV) was calculated to be smaller than those of **2b** (1.80 eV) and **12** (1.78 eV), and comparable to that of **2a** (1.66 eV). Furthermore, the smallest HOMO–LUMO gap of 1.25 eV was calculated for **9**. Our previous report attributed the small HOMO–LUMO gap of **2a** to an active conjugative involvement of the inserted carbonyl group.[2] In the cases of **3** and **9**, however, the Kohn–Sham orbital representations show no involvement of the inserted 1,2-phenylene parts in the HOMOs and LUMOs (Figure 4b,c), which is rather similar to methylene-bridged arch-tape dimer **2b**. As compared with **2b**, the HOMOs of **3** and **9** are destabilized by 0.090 and 0.334 eV, respectively, and the LUMOs are stabilized by 0.081 and 0.217 eV, respectively (Figure 4a). These results suggest that the increase of molecular contortion significantly decreases the HOMO–LUMO gap.

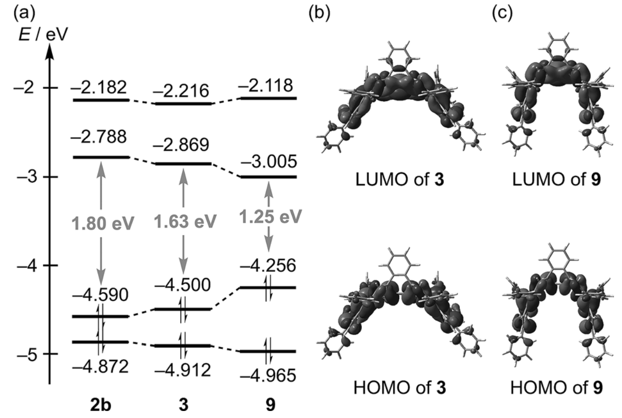
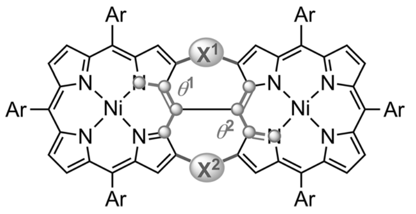


Figure 4. a) Energy diagrams of **2b**, **3**, and **9**. Kohn–Sham orbital representations of the HOMO and LUMO of b) **3** and c) **9**. All of the calculations were performed at the B3LYP/6-31G(d) (for C,H,N) + LANL2DZ (for Ni) level. *tert*-Butyl groups were replaced to hydrogen atoms to simplify the calculations.

Investigation into the effect of structural curvature on electronic properties of π-electronic systems has been an attractive research topic in modern physical organic chemistry. Bodwell and co-workers actively explored curved pyreneand teropyrene-derivatives with changing the degree of curvature.[14] Especially, they revealed that the HOMO–LUMO gaps of curved teropyrene-derivatives were widened as the molecular curvature increased, which is opposite to the trend observed in the present research.[14b] Thus, the observed tendency that more contorted porphyrin arch-tape dimers exhibited narrower HOMO–LUMO gaps is characteristic of the porphyrin arch-tapes.

The stabilization of LUMO is attributable to more effective through-space interaction between the β-positions accompanied with the decrease of a dihedral angle between the two porphyrin planes. Indeed, overlap of π-orbitals at the β-positions became larger in **9** rather than **3** (Supporting Information, Figure S80). Meanwhile, it is known that structurally distorted porphyrins exhibit higher HOMO levels.[15] Marchon, Medforth, Shelnutt, and co-workers claimed that interrupted bonding interaction between the *meso*- and α-positions should be responsible for HOMO destabilization.[16] Indeed, the HOMOs of various distorted porphyrins have been demonstrated to be more destabilized as a C_α–C_{meso}–C_α–N torsion angle θ increases. The θ values and HOMO energy levels of **2b**, **3**, **9**, and **12** in the optimized structures are summarized in Figure 5. These results suggest that the HOMO levels become more destabilized as the θ values increase. Namely, the introduction of large inserted units between the β-positions results in large tilts of the neighboring pyrrole units, which remarkably destabilizes the HOMO levels of the porphyrins by interrupting the bonding interaction between the *meso*- and α-positions.



	X^1	X^2	θ^1 [°]	θ^2 [°]	E_{HOMO} [eV]
12	—	—	1		–4.679
2b	CH_2	—	23–25	6–9	–4.590
3	1,2-C_6H_4	—	35	6	–4.500
9	1,2-C_6H_4	1,2-C_6H_4	38–41		–4.256

Figure 5. C_α–C_{meso}–C_α–N torsion angles (θ^1 and θ^2) and HOMO energy levels of **2b**, **3**, **9**, and **12**. All calculations were performed at the B3LYP/6-31G(d) (for C,H,N) + LANL2DZ (for Ni) level. *tert*-Butyl groups were replaced to hydrogen atoms to simplify the calculations.

The arch-shaped structures of **2a** and **2b** were reported to capture C_{60} effectively.[2] Thus, we examined the complexation behaviors of **3** and **9** with C_{60}. Addition of C_{60} to a dilute toluene solution of **3** caused distinct spectral changes (Supporting Information, Figure S81a). The complexation stoichiometry was confirmed to be 1:1 by Job's plot (Supporting Information, Figure S81b), and the curve fitting of $[C_{60}]_{total}$ versus ΔAbs at 922 nm gave an association constant K of $(1.07 \pm 0.02) \times 10^5$ L mol^{-1}, which is about ten times and three times larger than those of **2a** ($(1.03 \pm 0.02) \times 10^4$ L mol^{-1}) and **2b** ($(3.48 \pm 0.12) \times 10^4$ L mol^{-1}), respectively. These results indicate that the highly contorted structure of **3** is more suitable for the interaction with the curved π-surface of C_{60}. In contrast, addition of C_{60} to a dilute toluene solution of **9** caused no distinguishable spectral changes probably because the inner cavity of **9** is too narrow to capture C_{60} (Supporting Information, Figure S82).

The arch-tape dimer **2b** has been reported to undergo arch-to-arch inversion with a barrier of 13.3 kcal mol^{-1} at 30 °C.[2] To investigate the arch-to-arch inversion barrier of **3** and **9**, mesityl-substituted analogue **3Mes** and **9Mes** were newly prepared (Supporting Information, Scheme S2). Interestingly, the signals that are due to the *ortho*-methyl groups of the mesityl groups were observed as two sharp singlets at 2.13 and 1.57 ppm for **3Mes** and 1.99 and 1.60 ppm for **9Mes** even at 145 °C (Supporting Information, Figures S83 and S84). These results indicate that the arch-to-arch inversion barriers of **3Mes** and **9Mes** at 145 °C are higher than 20 kcal mol^{-1},[17] and they do not undergo arch-to-arch inversion on the NMR time scale at room temperature. The observed large activation energies can be attributed to the increased structural contortion.

In summary, 1,2-phenylene-inserted arch-tape dimers **3** and **9** were synthesized from β-to-β 1,2-phenylene-bridged porphyrin dimers **5** and **11**, respectively. Owing to the large structural strain imposed by the embedded eight-membered ring(s), **3** and **9** display more contorted structures as compared with carbonyl- and methylene-inserted arch-tape dimers **2a** and **2b**. As the molecular contortion increases, HOMO–LUMO gap becomes smaller, reaching at a remarkably small value in **9**. The DFT calculations have suggest that 1) the inserted 1,2-phenylene parts are not conjugated with the electronic networks of the porphyrins; 2) the effective through-space interaction between the phenylene-substituted β-positions stabilizes the LUMOs; and 3) the contorted structures cause the high-lying HOMO levels. Further attempts to explore novel arch-shaped porphyrin tapes by inserting different segments are actively in progress in our laboratory and will be reported elsewhere.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: curved π-conjugated networks · eight-membered rings · NIR-absorption · phenylenes · porphyrinoids

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[18] CCDC 1587765 (**3**), 1587764 (**6**), and 1824554 (**9**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Communications

Porphyrinoids

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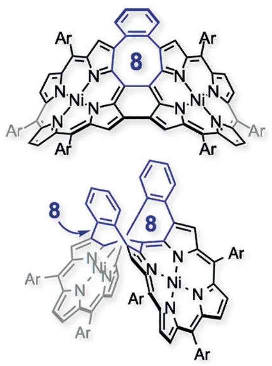
Singly and Doubly 1,2-Phenylene-Inserted Porphyrin Arch-Tape Dimers: Synthesis and Highly Contorted Structures



Arch-shaped Ni^{II} porphyrin tapes with single and double 1,2-phenylene insertions were prepared. These porphyrin arch-tapes display highly contorted structures owing to the presence of the embedded eight-membered ring(s). The more contorted doubly inserted dimer exhibits the lowest energy Q-band at 1294 nm and a remarkably small electrochemical HOMO–LUMO gap of 0.77 eV.