Multipyrrolic Macrocycles

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Cyclo[8]isoindoles: Ring-Expanded and Annelated Porphyrinoids**

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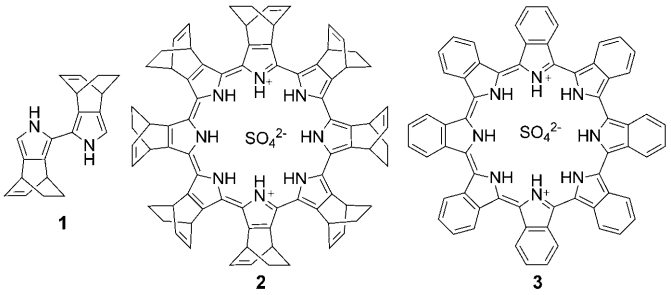
In recent years there has been a growing focus on the chemistry of ring-expanded porphyrins such as hexaphyrins and octaphyrins, because their properties differ markedly from those of conventional porphyrins in a manner that makes them potentially suitable for a number of novel practical applications.[1–5] Cyclo[8]pyrrole ([30]octaphyrin(0.0.0.0.0.0.0.0)), along with its smaller cyclo[6]- and cyclo[7]pyrrole analogues, was first reported by Sessler and co-workers based on an oxidative coupling of 2,2′-bipyrrole with $FeCl_3$.[6] A key structural difference with respect to the porphyrins is the complete absence of meso carbon atoms.[7] The photophysical,[5] anion-binding,[7a,b] and liquid-crystalline properties[7c] of cyclo[n]pyrroles ($n = 6$–8) have been studied in-depth, along with their electronic structures.[7d,8] The UV/Vis absorption spectra of cyclo[8]pyrroles contain a weaker band at approximately 430 nm ($\varepsilon \approx 1 \times 10^5\,\text{M}^{-1}\text{cm}^{-1}$) and a more intense band at approximately 1100 nm ($\varepsilon \approx 2 \times 10^5\,\text{M}^{-1}\text{cm}^{-1}$).[6a] The strong absorbance in the near-IR (NIR) region makes these compounds potentially suitable for use in optical storage and signaling devices. Despite the large variety of ring-annelated porphyrins that have been successfully synthesized,[9] there have been no reports of fused-ring-expanded cyclo[*n*]pyrroles, because the preparation of the required precursors is extremely challenging. To date, only β-alkyl substituted compounds have been prepared.[6,7] The ability to fine-tune the wavelengths of the major absorption bands based on structural modifications such as ring annelation would greatly enhance the utility of these compounds for practical applications. Herein, we report the first successful synthesis of cyclo[8]isoindole (**3**) based on an oxidative coupling of bicyclo[2.2.2]octadiene(BCOD)-fused 2,2′-bipyrrole (**1**), followed by the retro-Diels–Alder reaction of cyclo[8]BCODpyrrole (**2**; Scheme 1). We also report an in-depth analysis of the optical properties and electronic structures of **2** and **3** based on magnetic circular dichroism (MCD) spectroscopy and time-dependent (TD) DFT calculations.



Scheme 1. Structures of bipyrrole **1** and octaphyrins **2** and **3**.

Recently, we reported the synthesis of benzosapphyrins using the retro-Diels–Alder strategy to form fused-ring-expanded porphyrins from precursors with fused BCOD groups.[10] A similar strategy is adopted to synthesize cyclo[8]-isoindoles. The BCOD-fused 2,2′-bipyrrole **1** was prepared from BCOD-fused pyrrole according to literature procedures.[10a,11] Details of the synthesis of **2** under different conditions are summarized in Table 1. Initially, reaction conditions similar to those reported by Sessler and co-workers[6a] were adopted with a 1 M H_2SO_4 solution of $FeCl_3$ as the oxidant. In the procedure reported by Sessler and co-workers, the solution of **1** was slowly added to a mixture of the oxidant and acid over a period of 9 h by syringe pump. In contrast, we immediately added all of the $FeCl_3 \cdot 6H_2O$ oxidant and H_2SO_4 to a 2 mM solution of **1** in $CHCl_3$ and stirred the mixture for 45 minutes at 0 °C. After purification by silica gel column chromatography and gel permeation chromatography (GPC), **2** was obtained as deep blue crystals in 43% yield. The MALDI-TOF mass spectrum contained a molecular ion peak

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Table 1: Oxidative homocoupling of **1**.

Entry	Oxidant[a]	Acid	Additive	Yield
1	$FeCl_3 \cdot 6H_2O$	1 M H_2SO_4	None	43 %
2	$NaNO_2$	1 M H_2SO_4	None	24 %
3	$NaNO_2$	conc. H_2SO_4	None	40 %
4	$NaNO_2$	AcOH	None	21 %
5	CAN	AcOH	Na_2SO_4	28 %
6	AgO	conc. HNO_3	Na_2SO_4	41 %
7	$Ce(SO_4)_2$	6 M H_2SO_4	Na_2SO_4	54 %
8	$Ce(SO_4)_2$	6 M H_2SO_4	Na_2SO_4, $N(nBu)_4HSO_4$	68 %

[a] 0.1 M solution in H_2O (2 mL).

at $m/z = 1241$ with eight daughter peaks with successive mass differences of $m/z = 28$, which is consistent with the presence of eight BCOD-fused pyrroles.

Attempts were subsequently made to increase the yield by modification of the reaction conditions (Table 1). When the reaction was carried out using the nitrosonium ion (generated from $NaNO_2$ with acid) as a mild oxidant in 1M H_2SO_4 and concentrated H_2SO_4 solutions, lower yields of 24 and 40 %, respectively, were obtained (Table 1, entries 2 and 3). When acetic acid was used instead as part of an attempt to synthesize a free-base cyclo[8]BCODpyrrole, surprisingly, X-ray crystallography revealed that **2** was still obtained in 21 % yield after recrystallization from $MeOH/CHCl_3$ (Figure 1).[12] The sulfate ion was probably derived from the

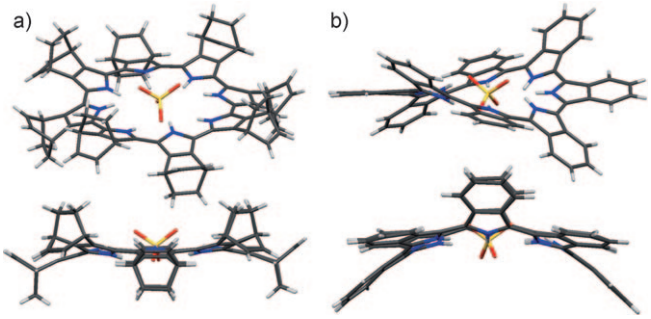

Figure 1. Top and side views of the molecular structures of a) **2** and b) **3** with solvent molecules omitted for clarity.

Na_2SO_4 used to dry the organic layer as part of the extraction process (entry 4). Cyclo[8]pyrroles have been reported previously to exhibit strong anion-binding properties.[7a–b] Since the SO_4^{2-} ion may be acting as a template for cyclization, Na_2SO_4 was added to the initial reaction mixture (entries 5–7). When cerium(IV) ammonium nitrate (CAN), AgO, and $Ce(SO_4)_2$ were used as oxidants, the yields were 21, 41, and 54 %, respectively, with $Ce(SO_4)_2$ in 6 M H_2SO_4 providing the best results. The addition of tetra(*n*-butyl)ammonium bisulfate as a phase-transfer catalyst further increased the yield obtained under these conditions to 68 % because of the template effect of the SO_4^{2-} anion (entry 8).

Thermogravimetric analysis was carried out to estimate the temperature at which the retro-Diels–Alder reaction of **2** occurs. Weight loss corresponding to the removal of eight ethylene molecules is observed to start at around 120 °C and is complete at 240 °C (see Figure S1 in the Supporting Information). When **2** was heated as a solid at 240 °C in a glass tube under reduced pressure, the color changed from blue to yellow and cyclo[8]isoindole (**3**) was formed in almost quantitative yield. Crystals suitable for X-ray structure determination were obtained after recrystallization from $CS_2/CHCl_3$. The crystal structures of **2** and **3** are shown in Figure 1 and 2 and the crystallographic data[12–15] are summarized in Table S1. In both cases, nonplanarity of the ligand and the geometry of the central SO_4^{2-} ion result in a D_{2d} molecular symmetry. The crystal structure of **2** is similar to that of the β-alkyl substituted cyclo[8]pyrroles reported by Sessler and co-workers[6a,7d] and contain a monoclinic cell, thus conforming to the $P2_1/c$ space group with $Z = 4$. Alternating pyrrole moieties tilt above and below the plane formed by the 16 α carbon atoms with a mean deviation of 0.1891 Å (Figure 2). In contrast, a mean displacement of

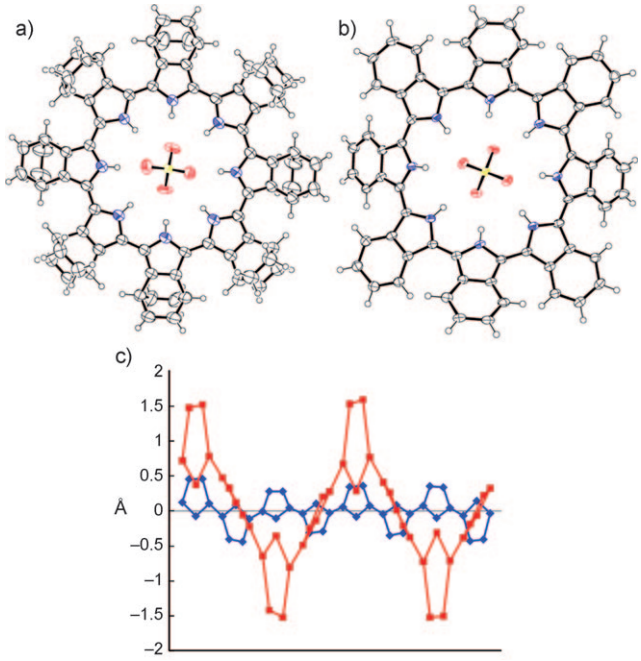

Figure 2. ORTEP drawing of a) **2** and b) **3**. Solvent molecules are omitted for clarity. c) Deviation from the mean cyclo[8]pyrrole planes of **2** (blue) and **3** (red).

0.4603 Å was reported for β-pyrrole-substituted cyclo[8]-pyrroles.[6a,7d] This observation is consistent with our previous reports that fused BCOD moieties enhance the level of planarity of porphyrinoid π systems.[16] Dihedral angles of 20.8–27.8° are observed between adjacent pyrrole moieties (Table S2), while the inner SO_4^{2-} ion is bound by six hydrogen-bonding interactions with NH···O distances ranging from 1.901 to 2.147 Å. Steric hindrance between the neighboring benzene rings of **3** at the ligand periphery results in a deeper saddling distortion of the cyclo[8]isoindole π system (Figure 1 and 2), which crystallizes in a monoclinic cell that conforms to space group *P*2/*c*. The mean deviation from the cyclo[8]pyrrole plane is 0.6081 Å, more than three times higher than the value for **2**. The dihedral angles between

adjacent pyrroles of 20.5–29.0° are similar, however. There is a slight bending of the isoindole moieties with dihedral angles of 1.98–2.07° between the pyrrole and fused benzene moieties (Figure 1).

The UV/Vis absorption and MCD spectra of **2** and **3** are shown in Figure 3 along with the results of the TD-DFT calculations (Table S3). There is a remarkable red-shift and relative intensification of the main absorption band in the visible region of the absorption spectrum upon fused-ring-expansion, which can readily be explained based on an analysis of the MCD data. Many of the key breakthroughs in understanding the electronic structures of porphyrinoids have been derived from MCD spectroscopy based on an analysis of the Faraday $\mathscr{A}_1$, $\mathscr{B}_0$, and $\mathscr{C}_0$ terms.[17] Since it is currently not possible to calculate MCD spectra using commercial DFT software packages, older approaches such as Michl's perimeter model[18] continue to play a major role. Michl demonstrated that the relative intensities of the main electronic absorption bands of aromatic π systems can be described in terms of structural perturbations to a high-symmetry parent hydrocarbon, since the nodal patterns of the π-system molecular orbitals (MOs) are retained even after the symmetry of the cyclic perimeter is modified.

The optical properties of cyclo[8]pyrroles can be understood with reference to a $C_{24}H_{24}^{6-}$ parent hydrocarbon that corresponds to the inner ligand perimeter with MOs arranged in an $M_L = 0, \pm 1, \pm 2, \ldots, \pm 10, \pm 11, 12$ sequence in ascending energy. The highest occupied molecular orbital (HOMO) and HOMO-1 of **2** and **3** have $M_L = \pm 7$ nodal properties, while $M_L = \pm 8$ nodal patterns are observed for the lowest unoccupied molecular orbital (LUMO) and LUMO + 1 (Figure 4). This result leads to an allowed B band and a forbidden L band with "$\Delta M_L = \pm 1$" and "$\Delta M_L = \pm 15$" properties, respectively. As was reported by Gorski et al.[7d] in the context of β-alkyl substituted cyclo[8]-pyrroles, the bands of **2** and **3** in the near IR and visible region can be assigned to the L and B transitions. There is a marked intensification of the L band relative to the B band in the MCD spectrum (Figure 3), because the MCD intensity mechanism is based on the relative magnitudes of the

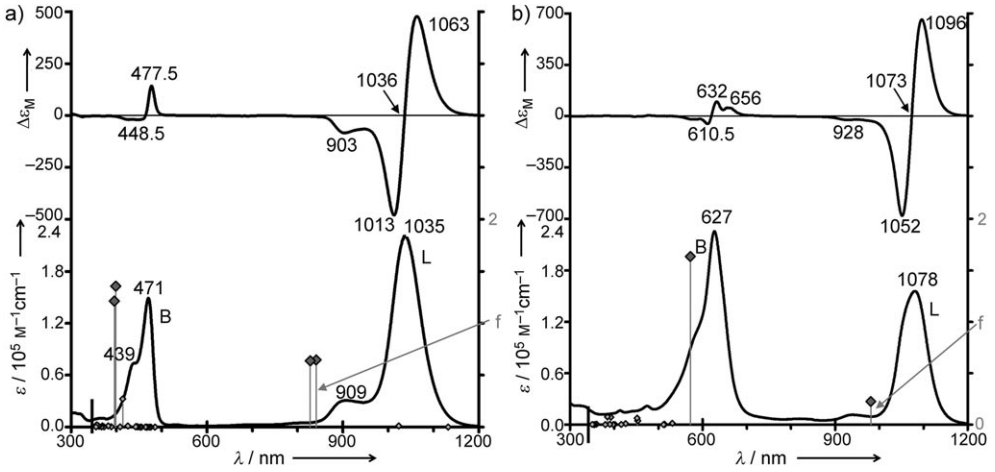

Figure 3. MCD (top) and absorption (bottom) spectra for a) **2** and b) **3**. Calculated TD-DFT spectra (Table S3) of the X-ray structures of **2** and **3** are plotted against the right-hand axes.

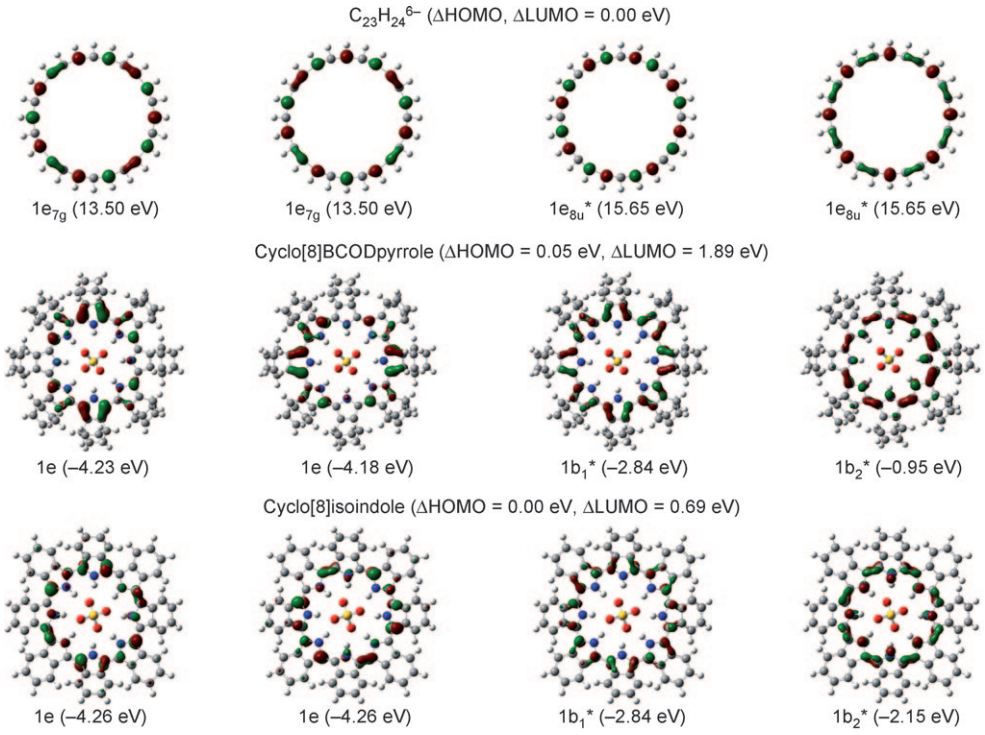

Figure 4. Nodal patterns, symmetry labels, and energies of the four frontier π MOs of $C_{24}H_{24}^{6-}$ and the X-ray structures of **2** and **3** at an isosurface value of 0.04 atomic units (hartrees). D_{2d} symmetry is assumed for **2** to simplify comparison of the TD-DFT results of **2** and **3** (Table S3).

magnetic moments of the ππ* excited states.[17] The MCD spectrum of **3** is dominated by derivative-shaped Faraday **&Ascr$_1$** terms because of the Zeeman splitting of the ^{1}E ππ* states. The spectrum of **2** differs somewhat from that reported by Gorski et al.,[7d] as there is a slight lifting of the degeneracy of the HOMO and HOMO-1 (Figure 5), which is due to a minor deviation from the D_{2d} symmetry. In the region of the B band, the derivative-shaped negative **&Ascr$_1$** term is replaced by an intense positive Faraday $\mathscr{B}_0$ term followed by a broad envelope of weaker overlapping negative $\mathscr{B}_0$ terms at higher energy (Figure 3).

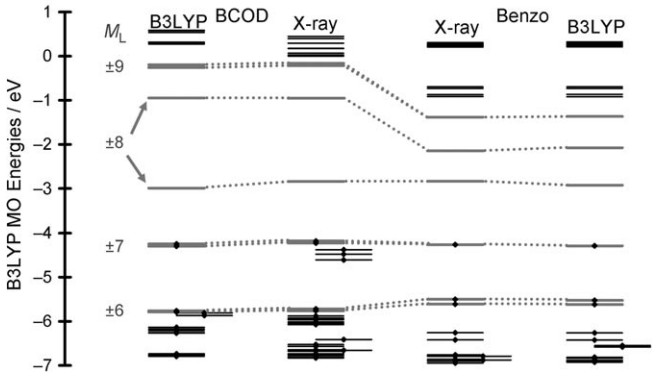

Figure 5. MO energies of **2** (left) and **3** (right) in TD-DFT calculations (Table S3) based on B3LYP geometry optimizations and the X-ray structures. MOs associated with the π MOs of the parent $C_{24}H_{24}^{6-}$ cyclic perimeter are highlighted in light gray and denoted by the relevant M_L value. MOs associated with the central SO_4^{2-} ion are offset to the right. The symmetry labels and MO energy values of the four frontier π MOs are given in Figure 4.

When a structural perturbation results in a splitting of the HOMO and/or LUMO of the parent perimeter (referred to as the ΔHOMO and ΔLUMO values by Michl[18], Figure 4), there is a mixing of the allowed and forbidden properties of the L and B bands and the L band can gain a significant intensity. When the C_{24} axis of $C_{24}H_{24}^{6-}$ is replaced by an S_4 improper rotation axis with respect to **2** and **3**, only the degeneracy of the $M_L = \pm 1, \pm 3, \pm 5, \pm 7, \pm 9, \pm 11$ MOs is retained. This means that, in contrast to the electronic structure of the D_{4h} symmetry porphyrinoids, in which the HOMO level is symmetry split and the degeneracy of the LUMO is retained, the LUMO levels of cyclo[8]pyrroles are symmetry-split, while the degeneracy of the HOMO level is retained. There is a relatively minor red-shift of the L band from 1035 to 1078 nm upon ring annelation (Figure 3), because the energies of the degenerate HOMO and the LUMO remain almost constant (Figure 5). In contrast, there is a marked red-shift of the higher energy B band from 471 to 627 nm, which is due to a marked stabilization of the LUMO + 1 (Figure 5 and Table S3). The ΔLUMO value predicted for **3** is, therefore, significantly lower than that predicted for **2** (Figure 4 and Table S3). As a result, the absorption intensity of the L band is significantly weaker relative to the B band (Figure 3) because there is less mixing of the forbidden and allowed properties of the L and B bands since there is a smaller perturbation compared to the structure of the $C_{24}H_{24}^{6-}$ parent perimeter.

The spectral changes observed when benzene rings are added to the structure of cyclo[8]pyrrole differ markedly from those observed for fused-ring-expanded porphyrins such as tetrabenzoporphyrins (TBPs) and tetranaphthoporphyrins (TNPs), in which it is the lower energy Q band (the name used for the L band in Gouterman's 4-orbital model[19]) that undergoes a marked red-shift and intensification.[20] This difference can be readily explained using Michl's perimeter model,[18] as the nodal properties of the frontier π MOs determine whether ring annelation results in a stabilization or a destabilization of the MOs. The difference in the energies of the LUMO and LUMO + 1 of **2** and **3** and the resulting decrease in the ΔLUMO value is related to the presence and absence, respectively, of nodal planes through the eight pyrrole nitrogen atoms and the peripheral fused rings (Figure 6). In contrast, similarly aligned nodal planes are predicted in the symmetry-split HOMO and HOMO-1 of porphyrin, TBP, and TNP (Figure S2), thus primarily resulting in a destabilization of the $1a_{1u}$ HOMO and hence in a decrease of the HOMO–LUMO band gap, an increase in the ΔHOMO value, and a red-shift and intensification of the Q band.[20]

The fluorescence emission spectra of **2** and **3** are shown in Figure S3 (see the Supporting Information). The fluorescence emission bands of **2** and **3** appeared at approximately 1090 and 1100 nm and were excited at 465 and 635 nm, respectively. Their Stokes shifts are smaller than those of β-alkyl cyclo[8]pyrroles[21] and the fluorescence lifetimes are estimated to be less than 0.1 ns.

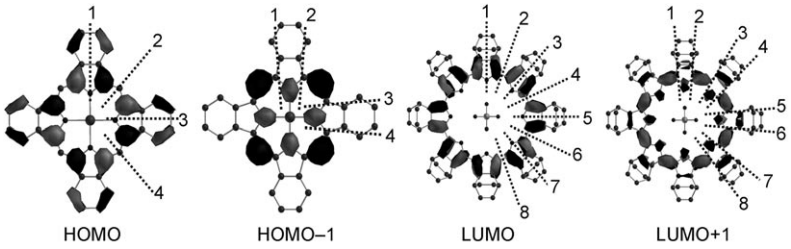

Figure 6. Nodal patterns of the HOMO and HOMO-1 of TBP (left) and the LUMO and LUMO + 1 of **2** (right) at an isosurface value of 0.025 atomic units (hartrees) with the $M_L = \pm 4$ and ± 8 nodal plane properties highlighted.

In summary, we have successfully synthesized a cyclo[8]-isoindole, based on the retro-Diels–Alder reaction of a BCOD-fused cyclo[8]pyrrole. Since several other fused ring moieties can be formed using this strategy, the synthesis of a wide range of novel cyclo[8]pyrroles should now be possible. Further studies are currently underway to investigate this possibility. X-ray crystallographic analysis revealed that while **2** has a near-planar structure, there is a marked saddling of the π-system of **3** because of steric hindrance at the ligand periphery caused by the lack of meso carbon atoms. Trends typically observed in the spectra of D_{4h} symmetry porphyr-

inoids do not apply to cyclo[8]pyrroles, since the alignment of the nodal planes of four key frontier π MOs are markedly different because of the expansion of the inner ligand perimeter and the absence of meso carbon atoms.[19] Peripheral benzo-substitution results in a marked relative intensification and red-shift of the B band to 627 nm because of a stabilization of the LUMO + 1. It can be demonstrated based on a perimeter model approach that further expansion of the π system is likely to move this band into the NIR region because of an even greater stabilization of the LUMO + 1. The unusual optical properties of fused-ring-expanded cyclo[*n*]pyrroles may prove to be suitable for a variety of different practical applications, such as use in photodynamic therapy, dye-sensitized solar cells, and as NIR dyes, which require strong absorbance and/or fluorescence in the 600–1200 nm region.

Experimental Section

Instrumentation: MALDI-TOF mass spectra were recorded on an Applied Biosystems Voyager de Pro. UV/Vis absorption spectra were measured on a JASCO V-570 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL AL-400 at 400 MHz. Elemental analyses were performed at the Integrated Center for Sciences, Ehime University. Geometry optimizations and TD-DFT calculations were carried out for **2** and **3** and the $C_{24}H_{24}^{6-}$ parent hydrocarbon perimeter by using the B3LYP functional with 6–31G(d) basis sets (Table S3).

General procedure for the oxidative coupling of **1**: Acid was added to a mixture of **1** (0.2 mmol) and any relevant additive (Table 1) in $CHCl_3$ (50 mL) at 0 °C and was stirred for further 5 min. After the slow addition of oxidant (0.1 M solution in H_2O), the mixture was stirred at 0 °C. The reaction mixture was then poured into water and the organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ as eluent to give **2**.

Cyclo[8]BCODpyrrole (**2**): deep blue crystals; UV/Vis (CH_2Cl_2): λ_{max} (logε) = 436 (shoulder, 4.87), 471 (5.17), 905 (4.49), 1035 nm (5.35); MS (MALDI-TOF): *m*/*z*: 1241 [M^+], 1213, 1185, 1156, 1128, 1100, 1072, 1044, 1016, 918.

Cyclo[8]isoindole (**3**): **2** was heated at 240 °C under reduced pressure for 3 h in a glass tube. **3** is formed in quantitative yields; yellow crystals; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 627 (5.39), 938 (4.05), 1078 nm (5.21); MS (MALDI-TOF): *m*/*z*: 1016 [M^+], 918; elemental analysis calcd (%) for $C_{64}H_{40}N_8SO_4$: C 75.57, H 3.96, N 11.02; found: C 75.59, H 4.03, N 10.96.

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