Light-Emitting Macrocycles

Synthesis and Light-Emitting Characteristics of Doughnut-Shaped π-Electron Systems**

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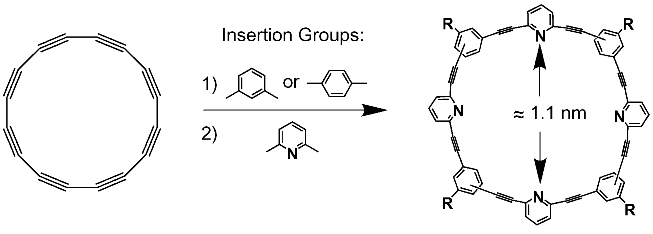
Molecular electronics owes its remarkable development in utilization to organic optoelectronic materials, and in particular, to light-emitting devices.[1] To date, many types of organic light-emitting material have been designed and fabricated for this purpose, most of which have a linear molecular shape, such as poly(*p*-phenylene vinylene). In addition to their optoelectronic applications, circular-shaped light-emitting molecules[2] may also be applicable in detecting circular-shaped nanodefects on the surface of materials. These possibilities have inspired us to create the doughnut-shaped light-emitting molecule **1**,[3,4] which is constructed by the formal insertion of pyridine and benzene groups into the single bonds of cyclohexadecayne, and to examine their light-emitting characteristics.



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Compounds **2** (abbreviated as octakis-*m*-cyclynes) and **3** (abbreviated as octakis-*p*-cyclynes) were synthesized by using the Sonogashira C–C coupling reaction[5] as the key step (Scheme 1). Thus, octakis-*m*-cyclyne **2** was obtained by the intramolecular cyclization of **6ac** (or **6bc**) under high dilution conditions, while octakis-*p*-cyclynes **3** were afforded by the intermolecular cyclization of **7ac** (or **7bc**), which have *p*-phenylethynyl units.

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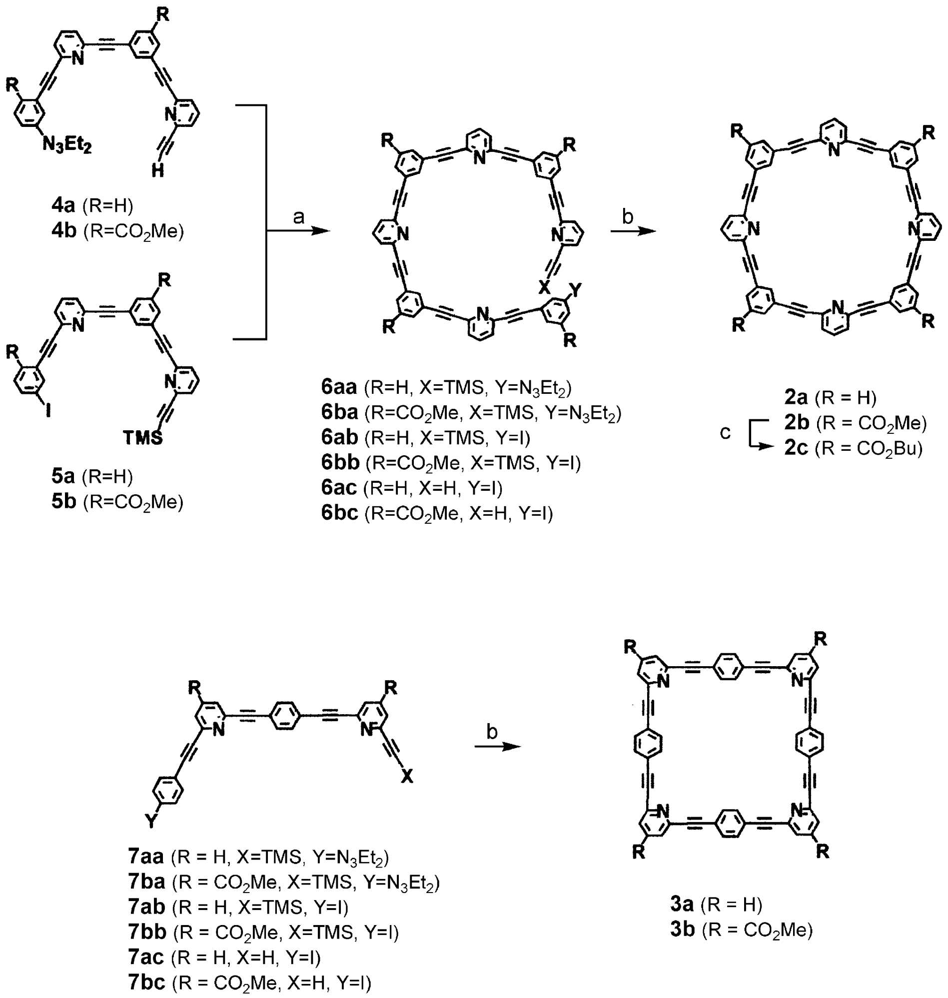
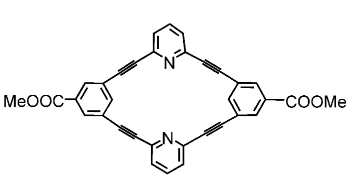


Scheme 1. Reagents and conditions: a) $[PdCl_2(Ph_3P)_2]$, CuI, Et_3N/THF (1:1), 53% (for **6aa**), 62% (for **6ba**); b) i) I_2, CH_2ClCH_2Cl, ii) KOH, MeOH, $CHCl_3$, iii) $[PdCl_2(Ph_3P)_2]$, CuI, Et_3N/THF (1:1), <5% (steps i–iii for **2a**), 35% (steps i–iii for **2b**), 11% (steps i–iii for **3a**), 5% (steps i–iii for **3b**); c) Na, BuOH, $CHCl_3$, 95% (for **2c**). TMS = trimethylsilyl.

Compounds **2** and **3** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (see Supporting Information). Although the ^{1}H and ^{13}C chemical shifts of the tetrakis-*m*-cyclynes **9** ($R = CO_2Me$)[4d] (strained system) appear at lower field (^{1}H shift of inner-ring protons: $\delta = 8.67$–8.85 ppm; ^{13}C shift of *sp* carbon atoms: $\delta = 89$–93 ppm) than is usually the case (strain-free system), the chemical shifts of **2** were observed at the same field as those of the acyclic homologue, 1,3-di(pyridylethynyl)benzene (**1,3-PBP**). This suggests **2** to be an almost strain-free system, in accordance with AM1 calculations. The AM1 calculation also suggests that the octakis-*p*-cyclynes **3** are also strain-free. The typical absorption and fluorescence spectra of **2b** and **3b** are shown in Figure 1, which demonstrates that the absorption maximum (λ_{abs}) and fluorescence maximum (λ_{em}) appears at longer wavelength for the *p*-cyclyne **3b** than for the *m*-cyclyne **2b**, although the difference ($\Delta\lambda_{abs} = 51$ nm, $\Delta\lambda_{em} = 49$ nm) is relatively small in spite of the *meta*-fused structure of **2b**.



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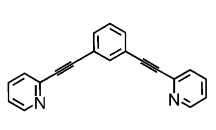

1,3-PBP

The photophysical data of **2**[6] and **3** are summarized in Table 1, together with other related systems. The table shows that not only long conjugated octakis-*p*-cyclynes (**3a**, **3b**), but also short conjugated octakis-*m*-cyclynes (**2b** and particularly **2c**) emit an unusually strong fluorescence, in contrast to the acyclic homologue **1,3-PBP**, whose λ_{abs} and λ_{em} values are nonetheless similar. ^{1}H NMR spectroscopy confirms that compounds **2** and **3** do not aggregate in chloroform solution (10^{-2} M–10^{-4} M). A small Stokes shift is also a characteristic photophysical property of these cyclynes.

It is noteworthy that compound **2b** can include two molecules of $[Cu^{II}(hfac)_2]$ (Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) provide the greenish-blue pentacoordinate Cu^{II} complex **8** upon standing in $CHCl_3$ for a week at room

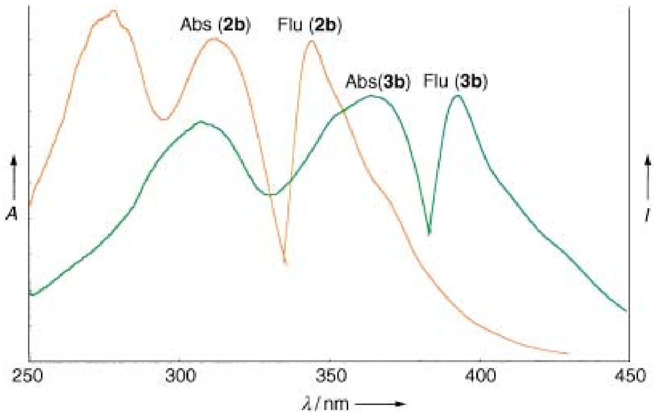

Figure 1. Absorption (Abs) and fluorescence (Flu) spectra of octakis-*m*-cyclyne **2b** and octakis-*p*-cyclyne **3b** in $CHCl_3$ (orange: **2b**; green: **3b**).

Table 1: Photophysical data of cyclynes and related compounds in $CHCl_3$.

Compound	λ_{abs} [nm]	$\log\varepsilon$	λ_{em} [nm]	$\Phi_f^{[a]}$	Stokes shift [nm]
2b[b]	315	5.19	344	0.18	29
2c[b]	313	4.92	344	0.37	31
3a[b]	334	5.13	371	0.59	37
3b[b]	366	4.27	393	0.33	27
8[b]	313	5.14	344	0.30	31
9[b]	322	4.64	356	0.11	34
1,3-PBP[b]	307	4.70	329	0.03	22

[a] Quantum yield is calculated relative to quinine ($\Phi_f=0.55$ in 0.1 M H_2SO_4). [b] $\lambda_{ex}=312$ (**2b**), 311 (**2c**), 333 (**3a**), 364 (**3b**), 313 (**8**), 311 (**9**), and 301 nm (**1,3-PBP**).

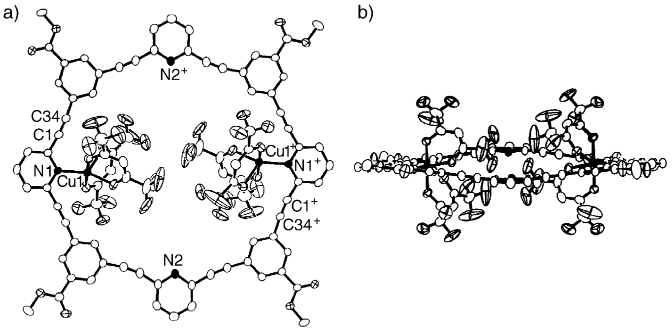

Figure 2. ORTEP representation of the pentacoordinate Cu^{II} complex **8**: a) front view, b) side view.

temperature. Its X-ray crystal structure (Figure 2; see also the Supporting Information) indicates that two opposing pyridine nitrogen atoms of **2b** coordinate to the Cu^{II} ions in $[Cu(hfac)_2]$, and that the cyclyne moiety has a coplanar structure with expected bond lengths and angles. The N···N separation between each Cu-coordinated pyridine ring is 15.56 Å and that between each free pyridine ring is 14.16 Å, while the Cu···Cu distance is 11.58 Å.

The Cu^{II} complex **8** emits remarkably strong fluorescence (Φ_f: 0.30 for **8**, 0.18 for **2b**), which is surprising as Cu^{II} ions are known to quench fluorescence. The reason for this observation is not clear at present. Complex **8** does not disassociate in solution, since the R_f value of complex **8** is quite different from that of parent **2b** in thin-layer chromatography (TLC) analysis with several solvents. Furthermore, the increase of quantum yield in complex **8** is definitive evidence that no dissociation takes place, because the quantum yield decreases in the solution of **2b** and $Cu(OTf)_2$. Therefore, the surprisingly high quantum yield of complex **8** seems to be a consequence of the inhibition of internal conversion, brought about by an increase in the rigidity of the cyclyne ring that stems from the steric-bulk effects of the Cu^{II}-coordinated hfac ligands.

In conclusion, the functionally and structurally interesting octakis-*m*-cyclynes **2** and octakis-*p*-cyclynes **3** are doughnut-shaped π-electron systems that are constructed by the formal insertion of pyridine and benzene groups into the single bonds of cyclohexadecayne. These doughnut-shaped azamacrocycles with cavity dimensions of ≈1 nm have strong light-emitting characteristics. In addition, the pentacoordinate Cu^{II} complex **8** of octakis-*m*-cyclyne **2b** emits remarkably strong fluorescence, contrary to scientific knowledge, which suggests that various transition-metal complexes of octakis-*m*-cyclynes **2** could be utilized to fabricate useful luminescent materials. The optoelectronic properties and other applications of the doughnut-shaped nano-fluorophores will be reported in due course.

Experimental Section

Phenyltriazane deprotection: A sealable flask was charged with the starting material (**6aa**, **6ba** or **7aa**, **7ba**), I_2 (1.2 equiv), and $ClCH_2CH_2Cl$.[7] The solution was degassed, back-filled with Ar, sealed, and stirred at 80 °C for 12 h. The reaction mixture was washed three times with 10% aqueous $Na_2S_2O_3$, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on SiO_2 (eluent: $CHCl_3$/EtOAc) to give the product (**6ab**, **6bb** or **7ab**, **7bb**).

(Trimethylsilyl)acetylene deprotection**:** The starting material (**6ab**, **6bb** or **7ab**, **7bb**) was dissolved in an approximate 10:1 mixture of $CHCl_3$ and MeOH with 2 M aqueous KOH (≈10 equiv), and the reaction mixture was stirred at room temperature. The reaction was monitored by TLC, and when the reaction was complete the reaction mixture was carefully washed with water. The organic fractions were then dried over $MgSO_4$ and evaporated. Chromatography on SiO_2 (eluent: $CHCl_3$/EtOAc) yielded the product (**6ac**, **6bc** or **7ac**, **7bc**).

Cyclization**:** A Schlenk flask charged with $[PdCl_2(Ph_3P)_2]$ (0.1 equiv) and CuI (0.05 equiv) was evacuated and back-filled with Ar three times. Then dry Et_3N and THF (2:1, v/v) was added to the flask. While the mixture was stirred under Ar at 75 °C, a solution of the sequence precursor (**6ac**, **6bc** or **7ac**, **7bc**) in dry THF was added to the flask by a syringe pump at a rate of $\approx 8\,mL\,h^{-1}$. After addition, the reaction mixture was stirred at the same temperature for 2 h and then the solvent was removed with a rotary evaporator. The product was purified by column chromatography on SiO_2 (eluent: $CHCl_3$/EtOAc and/or benzene/EtOAc) followed by recrystallization from $CHCl_3$. Spectral data of **2a**–**2c**, **3a**, and **3b** can be found in the Supporting Information.

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