

Synthesis and Photophysical Properties of Tris-bridged [3.3.*n*](3,6,9)Carbazolophanes

Keita Tani,^{*1} Naoki Sakumoto,¹ Koji Kubono,¹ Kazushige Hori,¹ Yasuo Tohda,¹ Hiroaki Benten,² Hideo Ohkita,² Shinzaburo Ito,² and Masahide Yamamoto³

¹Division of Natural Science, Osaka Kyoiku University, Asahigaoka, Kashiwara 582-8582

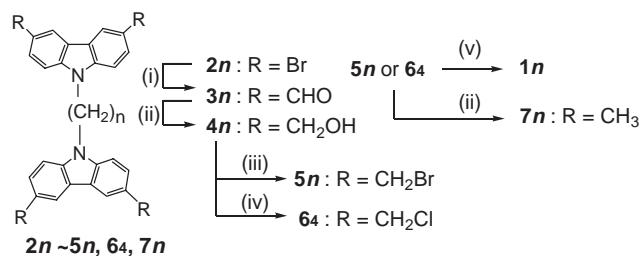
²Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510

³Faculty of Science and Engineering, Ritsumeikan University, Kusatsu 525-8577

(Received October 17, 2008; CL-081001; E-mail: ktani@cc.osaka-kyoiku.ac.jp)

Tris-bridged [3.3.*n*](3,6,9)carbazolophanes **1n** (*n* = 3–6), which are appropriate model compounds for fully overlapped excimer in carbazole chromophore, have been synthesized and characterized by NMR, X-ray, absorption and fluorescence spectra; **1n** showed excimeric fluorescence, whose emission maxima strongly depended on the angles and distances between carbazole rings.

Carbazole (Cz) chromophore has attracted intense interest since the discovery that poly(*N*-vinylcarbazole) shows photoconductivity.¹ Photophysical processes of the Cz chromophore have been the center of much attention from fundamental as well as application standpoints.² Poly(*N*-vinylcarbazole) afforded two types of excimer fluorescence, which were derived from sandwich (fully overlapped) and partially overlapped excimers.³ We have started our research project on elucidating the structure and properties of carbazole excimer by constructing suitable model systems, i.e., carbazolophanes,⁴ in which carbazole rings are fixed in distinct geometries. We have already prepared several bis-bridged [3.*n*](3,9)carbazolophanes and reported the structural requirements of partially overlapped excimer.⁵ Although the partially overlapped isomer was obtained in the cyanamide- and oxa-bridged cyclization or [2 + 2] photocyclization reaction, the fully overlapped isomer was not formed but *syn*-[2.4]- and *syn*-[3.3](3,9)carbazolophane in low yield.⁴ The synthesis and properties of the tris-bridged [2.2.*n*](3,6,9)carbazolophanes were firstly reported by Nishimura and co-workers,⁶ however, only [2.2.4]- and [2.2.5](3,6,9)carbazolophanes could be isolated probably owing to the strain by short linkage, which means that systematic research on fully overlapped excimer has not been achieved so far. We report here the synthesis, structure, and photophysical properties of tris-bridged [3.3.*n*](3,6,9)carbazolophanes **1n** (*n* = 3–6) (Chart 1), where two carbazole rings are basically fixed in face-to-face sandwich-like orientation, to investigate the properties of fully overlapped excimer in Cz chromophore.



Scheme 1. Reagents and conditions: (i) BuLi, -78°C , DMF; (ii) NaBH₄; (iii) HBr; (iv) HCl; (v) NH₂CN, NaOH.

The synthetic route of **1n** (*n* = 3–6) is shown in Scheme 1. Treatment of α,ω -bis(3,6-dibromocarbazol-9-yl)alkanes **2n** with butyllithium at -78°C , then with DMF to afford tetraaldehydes **3n**⁷ in 70–85% yields, which were reduced with NaBH₄ to yield tetraalcohols **4n**⁸ in 60–70% yields. Bromination of **4n** with concd hydrobromic acid in dichloromethane, which is very effective for the synthesis of bromomethyl carbazole derivatives, gave **5n** (*n* = 3, 5, and 6) in high yields. Inadequate bromination occurred in the case of **44**, probably owing to low solubility of both **44** and **54**. In place of **54**, tetrachloride **64** was prepared in 93% yield from **44** and concd hydrochloric acid. They were employed for the next cyclization reaction immediately, because tetrahalides **5n** (*n* = 3, 5, and 6) and **64** were unstable and easily decomposed to polymeric materials. As tetrasubstituted dicarbazolylalkanes **3n**, **4n**, **5n**, and **64** have not been reported so far, it is expected that many interesting multifunctional tetrasubstituted carbazole derivatives will be synthesized by conversion of these functional groups. The intramolecular cyclization of **5n** (*n* = 3, 5, and 6) or **64** with NH₂CN⁹ gave **1n**⁸ in 6.1–31%. Reference tetramethyl derivatives **7n** were prepared by the reduction of **5n** (*n* = 3, 5, and 6) or **64** with NaBH₄.

All tris-bridged carbazolophanes **1n** synthesized here afford good single crystals suitable for X-ray analysis by recrystallization.¹⁰ As typical examples, the molecular structures of **13** and **16** are shown in Figure 1. The intramolecular distances of non-bonded aromatic atoms between upper and lower carbazole rings in **13** are within the range of 3.15–3.49 Å, and their least-squares planes are inclined only 2.5°. These results apparently indicate that in **13** the π -electron repulsion is small and the

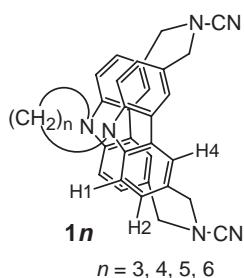


Chart 1.

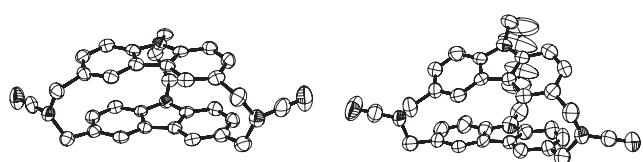


Figure 1. Molecular structures of **13** (left) and **16** (right).

two carbazole rings not only take parallel orientation but also situate at the appropriate distances for interaction between carbazole rings. Therefore, it was confirmed that [3.3.3](3,6,9)-bridged framework of **13** will be an ideal model compound for investigating the fully overlapped interaction in Cz chromophore. While in **16**, where two carbazole rings are connected by the longest alkylene chain, their least-squares planes are inclined as much as 33.1° , and the distance between nitrogen atoms in the carbazole ring is 5.02 \AA . Reflecting the difference of alkylene chain, the angles stated above in **14** and **15** are 17.2 and 30.1° (31.1°),¹¹ respectively.

The structure of **1n** in solution was also characterized by ^1H NMR. Chemical shifts of aromatic protons in **1n** essentially shifted upfield relative to the corresponding reference **7n**, due to the magnetic anisotropic effect of the faced carbazole ring. For example, H1, H2, and H4 in [3.3.4](3,6,9)carbazolophane **14** shifted upfield compared with those in **74** by 0.28, 0.13, and 0.18 ppm, respectively. These upfield shifts are due to the magnetic anisotropic effect of opposite aromatic rings and reasonably interpreted by the structure disclosed by X-ray analysis. Therefore, it is proved that tris-bridged [3.3.3](3,6,9)carbazolophanes are appropriate model compounds for examining the fully overlapped interactions in Cz chromophore systematically.

The absorption spectra of **1n** ($n = 3-6$) and **7n** in THF are shown in (A) in Figure 2. The absorption shapes of **1n** are quite different from that of **7n**, i.e., broadening and red- or blue-shift were observed. In particular, the absorption tail was extended over 400 nm in **13**. These features were interpreted by Kasha's molecular exciton theory.¹²

The fluorescence spectra of **1n** were measured in THF at room temperature as shown in (F) in Figure 2. All tris-bridged carbazolophanes **1n** ($n = 3-6$) exhibit broad and structureless emission and large Stokes shift. These observations clearly indicate that the emission of **1n** is assigned as fully overlapped excimer. The emission maxima of **1n** are shifted to the longer

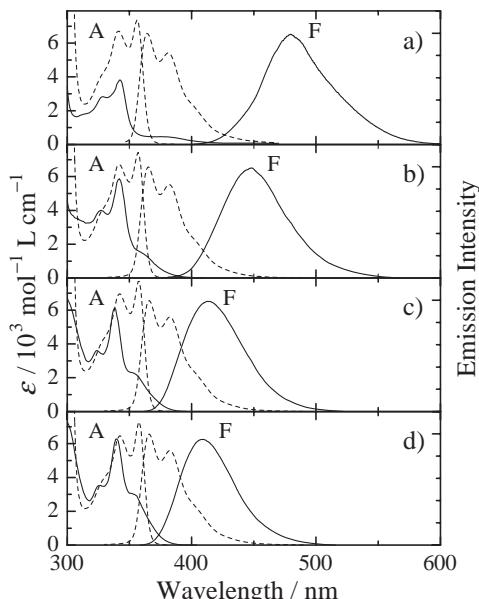


Figure 2. Absorption (A) and emission (F) spectra of **1n** (solid lines) and **7n** (broken lines) in THF at room temperature: a) **13** and **73**, b) **14** and **74**, c) **15** and **75**, d) **16** and **76**.

wavelength with shortening alkylene lengths, that is, those of **13**, **14**, **15**, and **16** are 480, 448, 414, and 409 nm, respectively. It was reported that a similar feature was also observed for [2.2.2](3,6,9)carbazolophanes.⁶ Therefore, it is demonstrated that the emission maxima of fully overlapped excimer are influenced by the angles and distances between two carbazole rings. It is also very interesting that poly(*N*-vinylcarbazole) emits sandwich (fully overlapped) excimer emission at 420 nm,³ which was nearly equal to that observed in **15**. These results suggest that the two carbazole rings forming sandwich excimer in poly(*N*-vinylcarbazole) might be also inclined.

In summary, tris-bridged [3.3.3](3,6,9)carbazolophanes **1n** ($n = 3-6$) were synthesized and the fluorescence spectra of them showed the formation of fully overlapped excimer. Further discussion on the structure and properties of fully overlapped excimer will be reported in future.

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- 8 ^1H NMR, elemental analyses or HRMS data, and mps of **1n** and **4n** were summarized in Supporting Information.¹³
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- 10 Crystallographic data of **1n** ($n = 3-6$) have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-710395 for **13**, CCDC-710396 for **14**, CCDC-710397 for **15**, and CCDC-710398 for **16**. Crystal data of **1n** ($n = 3-6$) are summarized in Supporting Information.¹³
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