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Synthesis and fluorescence emission behavior of novel *anti*-[2.*n*](3,9)phenanthrenophanes

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Abstract

Novel *syn*- and *anti*-[2.*n*](3,9)phenanthrenophanes (*n*=3,4) were successfully prepared by the intramolecular [2+2] photocycloaddition of α,ω-bis(3-vinyl-9-phenanthryl)alkanes. The *anti*-isomer of *n*=3 was found to give excimer fluorescence in spite of the only partially overlapping phenanthrene rings, although that of *n*=4 gave monomer fluorescence. © 2000 Elsevier Science Ltd. All rights reserved.

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In contrast with aromatic hydrocarbons such as benzene, naphthalene, and pyrene, phenanthrene fails to give excimer fluorescence in solution.[1] Even 1,3-diphenanthrylpropanes mainly afford monomer fluorescence,[2] contrary to Hirayama's rule.[3] We have succeeded in the first observation of excimer fluorescence almost free from monomer fluorescence at room temperature for *syn*-[2.2](1,6)phenanthrenophanes **1** whose phenanthrene rings are held almost in parallel.[4] For phenanthrene, however, the relationship between the arrangement of aromatic nuclei and fluorescence behavior has so far hardly been clarified, mainly due to the difficulty in the synthesis and separation of model compounds. In particular, the fluorescence for *anti*-phenanthrenophanes in which the phenanthrene rings only partially overlap had been unknown until our recent reports on *anti*-**2**,[5] although Staab et al. observed excimer fluorescence from a mixture of *syn*- and *anti*-[2.2](2,7)phenanthrenophane in a fluorene host crystal at 4.2 K.[6,7] Surprisingly, *anti*-**2** also provided excimer fluorescence with a slight blue-shift relative to *syn*-**2**.[5] This result prompted us to examine *anti*-phenanthrenophanes consisting of phenanthrene rings which overlap even less with each other and to clarify the minimum overlap essential for the formation of excimer. Here we report the preparation of *anti*-[2.*n*](3,9)phenanthrenophanes **3** (*n*=3, 4), regarded as a candidate for such phenanthrenophanes, by the intramolecular [2+2] photocycloaddition of the corresponding vinylphenanthrene derivatives **4** and their fluorescence behavior at room temperature.

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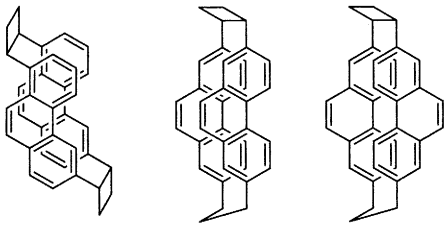
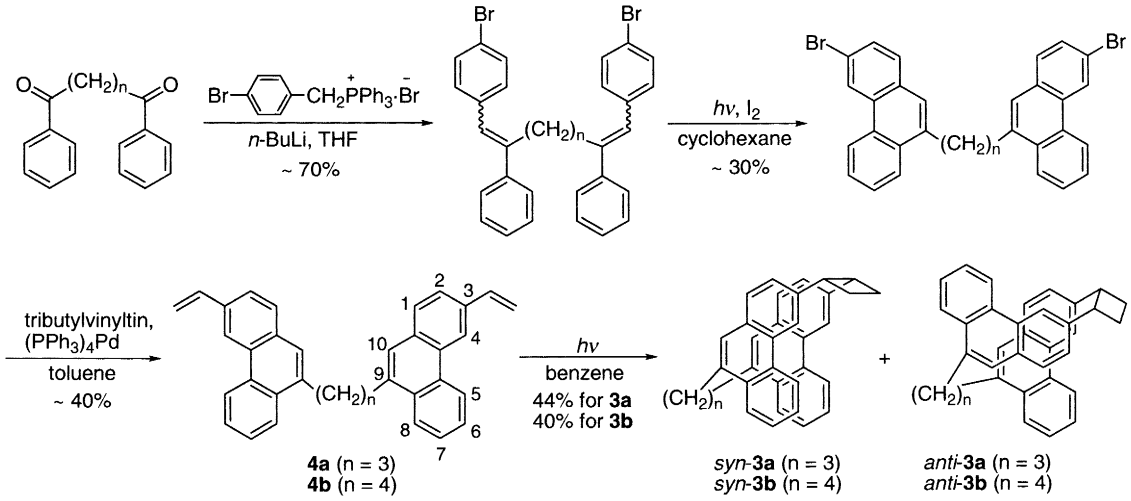


1 *syn*-**2** *anti*-**2**

α,ω-Bis(3-vinyl-9-phenanthryl)alkanes **4a** and **b** were prepared by a synthetic sequence entirely different from that for the precursor of **2**, as shown in Scheme 1, which utilizes the photochemical transannular reaction of stilbene derivatives as a key step. The intramolecular photoreaction of **4a** and **b**, carried out in benzene (2 mM) using a 400 W high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere, gave **3a** and **b** in 44 and 40% yields, respectively, as a mixture of *syn*- and *anti*-isomers. The *syn*:*anti*-isomer ratios were determined as ca. 1:6 and 1:3 for **3a** and **b**, respectively, on the basis of the peak areas of ^{1}H NMR spectra. No interconversion between the two isomers was observed at room temperature for at least several months.



Scheme 1.

Each isomer of **3a** and **b** was successfully separated by repeated GPC and/or HPLC. Their structures were mainly determined by ^{1}H NMR spectroscopy.[8] In *syn*-**3a**, only eight sets of aromatic proton peaks are observed and are generally high-field shifted compared to those of **4a**. The two methine protons of the cyclobutane ring appear as an equivalent peak. These results apparently indicate the *syn*-conformation where the two chromophores are well overlapped. The configuration of the cyclobutane ring was determined as depicted in Scheme 1 on the basis of a NOESY experiment; NOE interaction is detected between the cyclobutane methylene protons and H4 protons of the phenanthrene ring.[9] On the contrary, the ^{1}H NMR spectrum of *anti*-**3a** suggest a lower symmetrical structure; sixteen peaks are observed for the aromatic protons and two peaks for the methine protons. Among the aromatic protons, H1, H2, H4, H5, and H10 are high-field shifted relative to **4a**, while H6–8 are hardly shifted. Especially, the H10 (δ 5.99, 6.03) and H1 protons (δ 6.47, 6.63) in *anti*-**3a** resonate at higher fields than those in *syn*-**3a** (H10: δ 6.99; H1: δ 6.98), indicating that these protons are located above the opposite phenanthrene ring. Therefore, *anti*-**3a** is expected to adopt a conformation where one six-membered ring

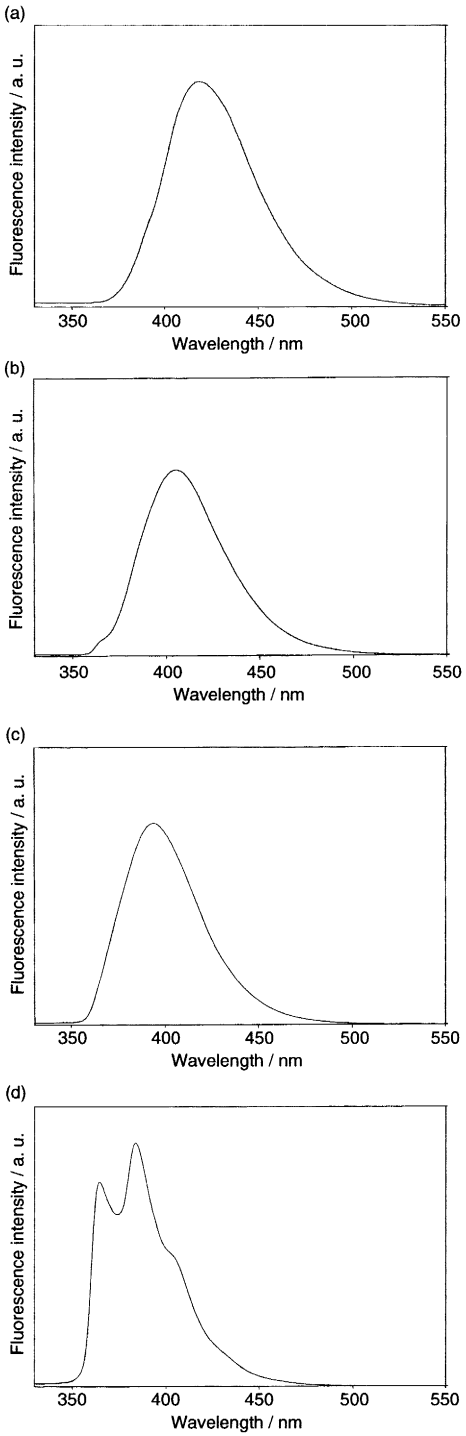


Fig. 1. Fluorescence spectra of: (a) *syn*-**3a**; (b) *anti*-**3a**; (c) *syn*-**3b**; and (d) *anti*-**3b** in cyclohexane at room temperature upon 280 nm excitation

of one phenanthrene nucleus is mainly overlapped with that of the other phenanthrene nucleus. The ^{1}H NMR spectral patterns of *syn*- and *anti*-**3b** are similar to those of *syn*- and *anti*-**3a**, respectively. The optimized structures of **3a** and **b** were determined by the MM2 calculations,[10] since single crystals suitable for X-ray crystallographic analysis have not been obtained. The two phenanthrene rings are arranged almost in parallel for both isomers of **3a**, but they differ in the extent of their overlap; in *anti*-**3a**, they are partially overlapped in the manner described above, whereas they are fully overlapped in *syn*-**3a**.

The absorption spectra of *syn*- and *anti*-**3a**,**b** in cyclohexane exhibit considerable broadening and a red-shift in comparison with that of phenanthrene.[11] Among these phenanthrenophanes, however, we cannot find marked differences corresponding to the structural differences.

Fig. 1 illustrates the fluorescence spectra of *syn*- and *anti*-**3a**,**b** in cyclohexane at room temperature.[11] The spectrum of *syn*-**3a** is composed of a broad structureless emission, similar to that of **1** reported previously,[4] with a maximum at 420 nm red-shifted compared to **1** (410 nm). Interestingly, *anti*-**3a** also exhibits a similar broad emission without any vibrational structures, where the maximal position (407 nm) is remarkably blue-shifted relative to *syn*-**3a**. As far as can be judged from the appearance, it is reasonable to interpret these emissions as excimer fluorescence rather than monomer fluorescence, although some kinetic investigation is necessary for the precise assignment. The blue-shift in *anti*-**3a** relative to *syn*-**3a** is ascribed to the lower stabilization in the excimer due to the smaller overlap of the two aromatic rings. For *syn*-**3b**, similar broad structureless emission is observed with further blue-shift (λ_{max}=395 nm). This is also assignable as excimer fluorescence. The blue-shift in *syn*-**3b** relative to *syn*-**3a** is apparently derived from the difference in the bridging length; in the excited state of *syn*-**3b**, the two phenanthrene rings cannot approach each other as closely as in *syn*-**3a**. In contrast, *anti*-**3b** affords apparent vibrational structures characteristic of monomer fluorescence. The arrangement of *anti*-**3b** no longer appears to be favorable for the excimer formation.

In summary, we have succeeded in the preparation of *syn*- and *anti*-[2.*n*](3,9)phenanthrenophanes **3a** (*n*=3) and **3b** (*n*=4) by the intramolecular [2+2] photocycloaddition and the separation of both isomers. Surprisingly, excimer fluorescence was observed even for *anti*-**3a**, where the phenanthrene nuclei overlap mainly at the single six-membered ring.

Acknowledgements

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8. The spectral data of **3a** and **3b** are as follows: *syn*-**3a**: m.p.>300°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.09 (2H, d, *J*=7.3 Hz, H5), 7.74 (2H, s, H4), 7.65 (2H, d, *J*=7.0 Hz, H8), 7.15 (4H, m, H6 and H7), 6.99 (2H, s, H10), 6.98 (2H, d, *J*=8.0 Hz, H1), 6.59 (2H, d, *J*=8.0 Hz, H2), 4.43 (2H, m), 3.65 (2H, m), 3.01 (1H, m), 2.94 (2H, m), 2.78 (4H, m), 2.34 (1H, m);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.60, 133.67, 130.30, 129.83, 129.68, 129.59, 127.53, 126.62, 126.58, 125.18, 124.96, 124.08, 122.58, 121.79, 47.15, 34.53, 29.70, 26.82, 20.86; HRMS (FAB) calcd for $C_{35}H_{28}$ (M^+): 448.2191; found: 448.2189. *anti*-**3a**: m.p. >300°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.37 (1H, d, *J*=7.3 Hz, H5), 8.22 (1H, d, *J*=8.0 Hz, H5), 8.14 (1H, d, *J*=7.6 Hz, H8), 8.09 (1H, d, *J*=7.9 Hz, H8), 7.61 (4H, m, H6 and H7), 7.37 (1H, s, H4), 7.18 (1H, d, *J*=8.0 Hz, H2), 7.01 (1H, s, H4), 6.72 (1H, d, *J*=7.9 Hz, H2), 6.63 (1H, d, *J*=8.2 Hz, H1), 6.47 (1H, d, *J*=8.2 Hz, H1), 6.03 (1H, s, H10), 5.99 (1H, s, H10), 4.37 (1H, m), 4.24 (1H, m), 3.56 (2H, m), 2.80 (4H, m), 2.55 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.09, 136.66, 134.44, 134.26, 131.17, 131.04, 130.66, 130.46, 129.45, 129.39, 129.34, 129.19, 127.53, 125.80, 125.53, 125.32, 125.24, 125.16, 124.76, 124.57, 124.25, 124.23, 124.00, 123.33, 123.26, 121.30, 48.28, 46.76, 31.67, 31.50, 28.86, 21.09, 19.91; HRMS (FAB) calcd for $C_{35}H_{28}$ (M^+): 448.2191; found: 448.2184. *syn*-**3b**: m.p. >300°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.27 (2H, d, *J*=8.3 Hz, H5), 8.07 (2H, s, H4), 7.56 (2H, d, *J*=8.3 Hz, H8), 7.21 (2H, t, *J*=7.5 Hz, H6), 7.13 (2H, t, *J*=7.5 Hz, H7), 7.03 (2H, d, *J*=7.9 Hz, H1), 6.93 (2H, s, H10), 6.69 (2H, d, *J*=7.9 Hz, H2), 4.43 (2H, m), 3.15 (2H, m), 2.94 (2H, m), 2.78 (2H, m), 2.40 (2H, m), 1.84 (2H, m), 1.64 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.12, 135.96, 130.42, 130.00, 129.60, 128.77, 128.39, 126.73, 125.63, 125.33, 125.26, 123.81, 122.41, 121.26, 46.80, 31.80, 29.70, 30.46, 21.27; HRMS (FAB) calcd for $C_{36}H_{30}$ (M^+): 462.2348; found: 462.2351. *anti*-**3b**: m.p. 290°C (dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.42 (1H), 8.28 (1H), 7.95 (1H), 7.92 (1H), 7.58 (6H, m), 7.40 (1H, d, *J*=8.3 Hz, H2), 6.94 (1H, d, *J*=8.2 Hz, H2), 6.92 (1H, d, *J*=7.9 Hz, H1), 6.77 (1H, d, *J*=7.9 Hz, H1), 6.30 (1H, s, H10), 6.29 (1H, s, H10), 4.43 (1H, m), 4.29 (1H, m), 3.15 (2H, m), 2.99 (1H, m), 2.78 (1H, m), 2.65 (1H, m), 2.53 (1H, m), 2.23 (2H, m), 1.78 (2H, m), 1.55 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.80, 137.47, 135.96, 135.85, 131.61, 131.58, 130.11, 129.91, 129.44, 129.36, 128.57, 128.30, 127.49, 125.63, 125.59, 125.53, 125.50, 125.47, 125.14, 125.08, 124.68, 124.48, 124.45, 123.94, 123.79, 122.92, 122.86, 120.27, 47.94, 46.44, 31.29, 30.78, 30.63, 21.39, 20.28; HRMS (FAB) calcd for $C_{36}H_{30}$ (M^+): 462.2348; found: 462.2343.

9. The isomer possessing a cyclobutane ring directed to the H2-side seems to be only slightly formed, but its isolation and characterization has been unsuccessful.
10. MM2 calculations were performed by CS Chem 3D Pro Version 4.0 (Cambridge Soft Corporation).
11. The absorption and fluorescence spectra were measured for the solutions in the range of 10^{-5}–10^{-4} M. The fluorescence excitation spectra are in good agreement with the corresponding absorption spectra in all cases.