Excimer Fluorescence from *anti*-[2.3](2,7)Phenanthrenophane

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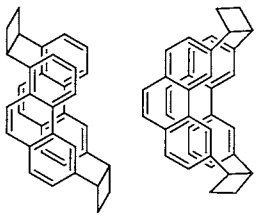
In the [2.3](2,7)phenanthrenophanes prepared by the intramolecular [2 + 2] photocycloaddition of 1,3-bis(7-vinyl-2-phenanthryl)propane, excimer fluorescence was observed for not only *syn*- but also *anti*-isomer, though the maximal position of the latter was slightly blue-shifted relative to the former.

Phenanthrene is known to give no excimer fluorescence in contrast with other aromatic hydrocarbons such as benzene, naphthalene, and pyrene.[1] In some 1,3-diphenanthrylpropanes, the fluorescence spectra are mainly composed of monomer fluorescence, and the contribution of excimer fluorescence is generally small.[2] Recently, we have reported that [2.2](1,6)phenanthrenophane **1** exhibited excimer fluorescence almost free from monomer fluorescence at room temperature, whereas [2.2](3,6)phenanthrenophane **2** gave only monomer fluorescence.[3] This spectral difference can be reasonably explained in terms of the difference in the arrangement of the two phenanthrene rings; they are kept almost in parallel for **1**, while arranged at the dihedral angle of ca. 40° for **2**. Since both **1** and **2** are essentially *syn*-phenanthrenophanes, we were prompted to examine the fluorescence of *anti*-phenanthrenophane where the two phenanthrene rings are only partially overlapped. Staab et al. synthesized [2.2](2,7)phenanthrenophane as a mixture of *syn*- and *anti*-isomers, whose separation was not achieved.[4] They observed excimer fluorescence for this mixture in a fluorene host crystal at 4.2 K, but the fluorescence of *anti*-phenanthrenophane remains unknown.[5] Thus, we attempted to synthesize *syn*- and *anti*-[2.3](2,7)phenanthrenophanes **3** by the intramolecular [2 + 2] photocycloaddition of a vinylphenanthrene derivative, separate both isomers, and examine their fluorescence behavior. In this paper, the fluorescence of an *anti*-phenanthrenophane is disclosed for the first time.



1 **2**

The precursor of phenanthrenophane, α,ω-bis(7-vinyl-2-phenanthryl)propane **4**, was prepared as shown in Scheme 1. The photoreaction of **4**, carried out in benzene (1 mM) using a 400-W high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere, gave **3** in 40% yield as a mixture of *syn*- and *anti*-isomers. The isomer ratio was determined on the basis of the peak areas of ^{1}H NMR spectra, and the *anti*-isomer was preferentially obtained (*syn*-**3**:*anti*-**3** = 1:1.3). No interconversion between both isomers was observed at room temperature for at least several months.

The two isomers of **3** were successfully separated by the reversed-phase HPLC. The structures of *syn*- and *anti*-**3** were mainly determined by ^{1}H NMR spectroscopy.[6] The aromatic protons of both *syn*- and *anti*-**3** are generally high-field shifted compared with those of **3** due to the shielding effect of the aromatic nuclei, obviously suggesting the formation of phenanthrenophanes. In *syn*-**3**, only eight sets of aromatic proton peaks are observed, corresponding to its symmetrical structure. The configuration of the cyclobutane ring was determined as depicted in Scheme 1 on the basis of NOESY experiment; NOE interaction was detected between the cyclobutane methylene protons and H1 protons of the phenanthrene ring.[7] On the contrary, *anti*-**3** gives a rather complex spectrum especially in the aromatic region due to the lower symmetry. The H4 and H5 protons in *anti*-**3** (δ = 7.49–7.63) resonate at higher fields than those in *syn*-**3** (δ = 7.78, 7.72), since these protons are located above the central benzene ring of the opposite phenanthrene ring. These features apparently indicate the formation of the *anti*-isomer. Although the X-ray crystallographic analysis has been

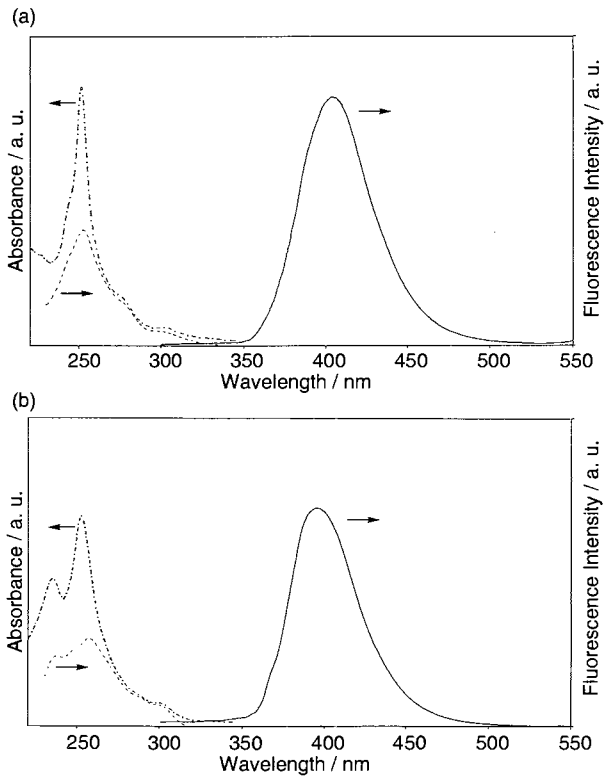
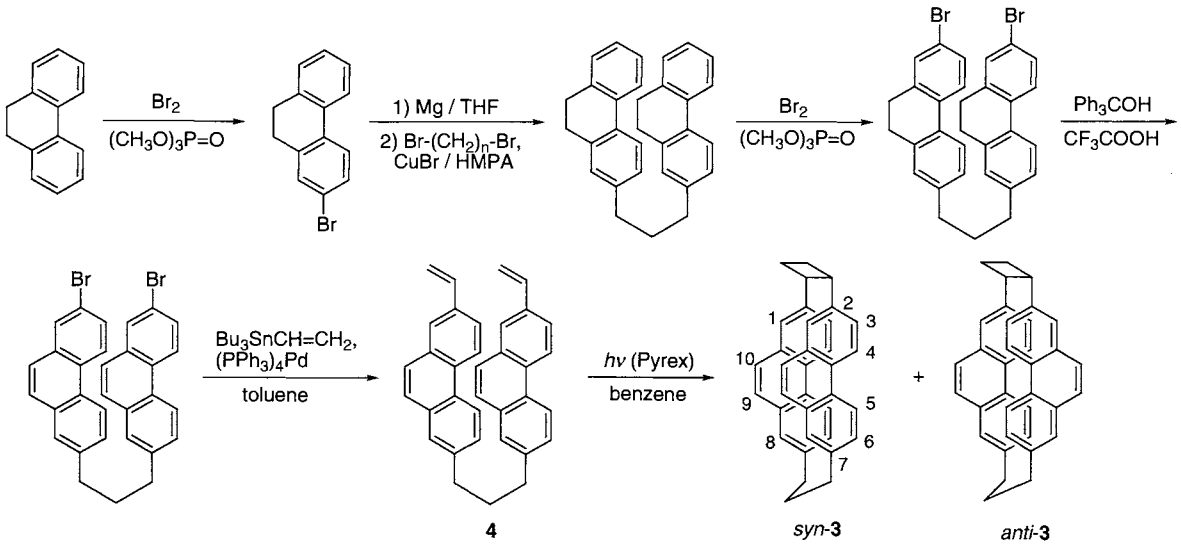


Figure 1. Fluorescence (—; λ_{ex} = 280 nm), absorption (– · –), and fluorescence excitation (– –; λ_{em} = 405 nm for *syn*-**3**, λ_{em} = 395 nm for *anti*-**3**) spectra of (a) *syn*- and (b) *anti*-**3** in cyclohexane at room temperature.



Scheme 1. Preparation of **3**.

unsuccessful for both isomers, the two phenanthrene rings are expected to be held almost in parallel according to the MM3 calculation.

Figure 1 shows the absorption and fluorescence spectra of *syn*- and *anti*-**3** in cyclohexane at room temperature. The absorption spectra of *syn*- and *anti*-**3** in cyclohexane exhibit considerable broadening and red shift in comparison with that of phenanthrene. The structural difference in both isomers, however, is not sufficiently reflected in their absorption spectra.

The fluorescence spectrum of *syn*-**3** is composed of a broad structureless emission with a maximum at 405 nm. This fluorescence, similar to that observed for **1**, can be assigned as excimer fluorescence. Interestingly, *anti*-**3** also exhibits a similar broad emission, though the maximal position (395 nm) is slightly blue-shifted relative to *syn*-**3**. It is also reasonable to interpret this emission as excimer fluorescence instead of monomer fluorescence. The blue shift in *anti*-**3** is ascribed to the less stability in the excimer of *anti*-**3** due to the smaller overlap of the two aromatic rings. The fluorescence excitation spectra of **3** are in good agreement with the corresponding absorption spectra, indicating that the observed fluorescence undoubtedly results from each compound.

In conclusion, we could prepare *syn*- and *anti*-[2.3](2,7)phenanthrenophanes by the intramolecular [2 + 2] photocycloaddition and separate both isomers. It was first proved that, when the two phenanthrene rings are arranged almost in parallel, not only the *syn*- but also *anti*-isomer can afford excimer fluorescence, though the λ_{max} depends on their arrangement.

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References and Notes

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6 The spectral data of *syn*-**3** and *anti*-**3** are as follows. *syn*-**3**: mp > 300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (2H, d, *J* = 8.5 Hz), 7.72 (2H, d, *J* = 8.6 Hz), 7.16 (2H, d, *J* = 8.6 Hz), 7.16 (2H, d, *J* = 1.8 Hz), 7.12 (2H, s), 7.06 (2H, d, *J* = 8.6 Hz), 7.00 (2H, d, *J* = 8.6 Hz), 6.64 (2H, dd, *J* = 8.5, 1.8 Hz), 4.34 (2H, m, cyclobutane methine), 3.07 (2H, m, $ArCH_2CH_2$), 2.89 (2H, m, $ArCH_2CH_2$), 2.71 (4H, m, cyclobutane methylene), 2.36 (2H, m, $ArCH_2CH_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.49, 137.82, 131.14, 130.62, 129.23, 128.41, 127.88, 127.27, 127.22, 126.59, 126.49, 126.44, 121.78, 121.71, 46.17, 30.51, 29.70, 20.88; MS (FAB) calcd for $C_{35}H_{28}$ (M^+) 448.2191; found 448.2173. *anti*-**3**: mp > 300 °C; ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.63 (1H, d, *J* = 8.6 Hz), 7.54 (1H, d, *J* = 8.2 Hz), 7.51 (1H, d, *J* = 8.5 Hz), 7.49 (1H, d, *J* = 8.6 Hz), 7.28 (1H, d, *J* = 8.8 Hz), 7.24 (1H, d, *J* = 8.8 Hz), 7.19 (1H, d, *J* = 8.8 Hz), 7.15 (1H, d, *J* = 8.8 Hz), 7.05 (6H, m), 6.69 (1H, d, *J* = 1.6 Hz), 6.67 (1H, dd, *J* = 8.5, 1.8 Hz), 4.32 (2H, m, cyclobutane methine), 2.95 (4H, m, $ArCH_2CH_2$), 2.70 (4H, m, cyclobutane methylene), 2.38 (2H, m, $ArCH_2CH_2$); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 139.07, 138.41, 138.18, 131.80, 131.60, 131.20, 131.15, 129.77, 128.59, 128.18, 128.15, 128.06, 128.01, 127.97, 127.76, 127.22, 127.19, 126.61, 126.46, 126.43, 126.34, 126.18, 125.68, 125.01, 121.00, 120.95, 120.79, 120.67, 47.08, 46.58, 36.71, 30.08, 21.21, 20.73; HRMS (FAB) calcd for $C_{35}H_{28}$ (M^+) 448.2191; found 448.2189.
7 The isomer whose cyclobutane ring is directed to the opposite side was not detected at all, though the origin of the selectivity is not clear. MM2, PM3, or AM1 calculation suggested no significant difference in the stability between both isomers.