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Synthesis and photoluminescence properties of some novel fluorenophanes

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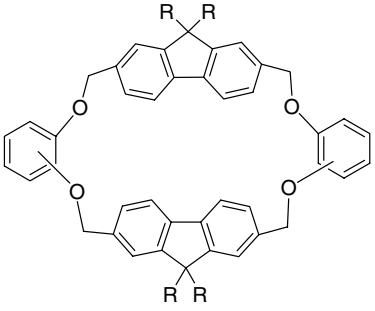
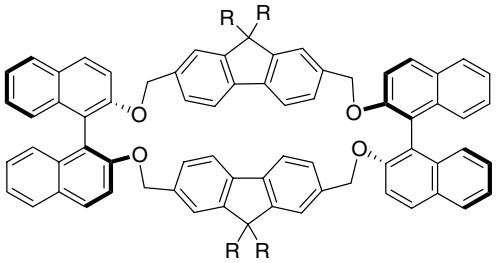
Abstract—Fluorenophanes derived from 2,7-bis-(bromomethyl)-9,9′-diheptyl-9*H*-fluorene and various diols exhibit excellent photoluminescence properties.

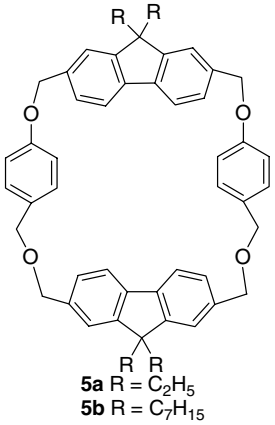
One of the most characteristic features of supramolecular chemistry is that it provides information about intermolecular and intramolecular interactions.[1] During the course of our studies on the synthesis of cyclophanes,[2,3] the fluorene unit was selected as the component of such cyclic compounds because of its remarkable fluorescent nature. Fluorene-based derivatives were extensively investigated for electronic and photonic applications, such as light emitting diodes,[4] charge-transfer agents,[5] field effect transistors,[6] sensors,[7] and more recently, two-photon absorbing materials.[8] The synthesis of 2,7-bridged fluorenophanes and their conformational studies were reported by Tsuge et al.[9] indicating the importance of the orientation between the fluorene component with reference to the other aromatic components.

We describe here the synthesis of 2,7-bridged fluorenophanes **1a**–**5a** and **1b**–**5b** consisting of *o*-, *m*-, and *p*-benzene diols and *S*-(−)-Binol units and their conformational, absorption and photoluminescence behavior.

The synthetic pathway leading to precyclophane **8b** is outlined as an example (Scheme 1). The reaction of 1.0 equiv of 2,7-bis-(bromomethyl)-9,9′-diheptyl-9*H*-fluorene **7b** with 2.5 equiv of catechol in dry acetone at rt gave precyclophane **8b** as a pale yellow solid in 62% yield. The ^{1}H NMR spectrum of **8b** showed a triplet







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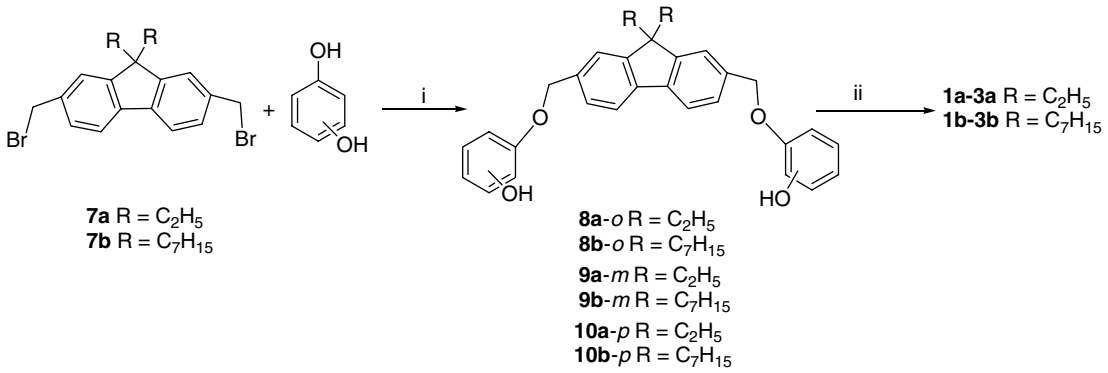


Scheme 1. Reagents and conditions: (i) K_2CO_3, dry acetone, rt, 48 h, **8a** (68%), **8b** (62%); **9a** (62%), **9b** (59%); **10a** (50%), **10b** (58%); (ii) **7a/7b**, K_2CO_3, dry acetone, rt, 120 h, **1a** (31%), **2a** (28%), **3a** (19%), **1b** (21%), **2b** (27%), **3b** (16%).

at δ 0.79 ($J = 7.34$ Hz) for the CH_3 protons of the aliphatic unit, a multiplet at δ 1.02–1.25 integrating for twenty aliphatic methylene protons, and a triplet at δ 1.94 ($J = 7.96$ Hz) integrating for four methylene protons attached to C-9 of the fluorene moiety. The *O*-methylene protons appeared as a singlet at δ 5.18 in addition to the aromatic protons. In the ^{13}C NMR spectrum, the aliphatic carbons of **8b** appeared at δ 14.3–40.4, the methylene carbon attached to C-9 of the fluorene moiety and the *O*-methylene carbons appeared at δ 55.1 and δ 66.9 in addition to the aromatic carbons.

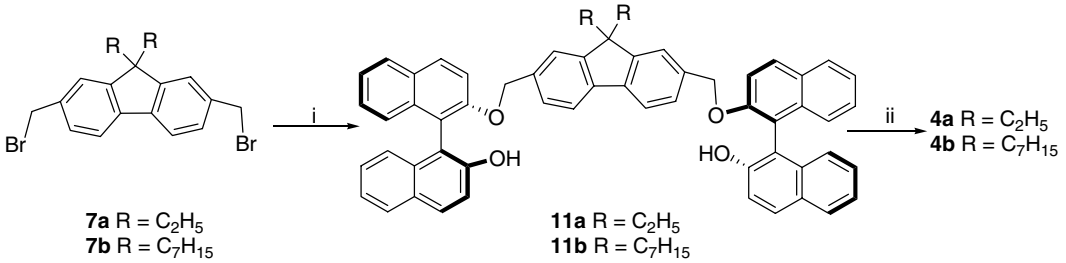
The synthesis of fluorenophane **1b** could be achieved under high dilution conditions. The reaction of 1.0 equiv of precyclophane **8b** with 1.0 equiv of **7b** in dry acetone at rt for 120 h afforded fluorenophane **1b** as a yellow solid in 21% yield. The ^1H NMR spectrum of compound **1b** showed a triplet at δ 0.80 ($J = 7.34$ Hz) for the 12 protons of the methyl groups of the aliphatic unit, a multiplet at δ 1.04–1.28 for the methylene protons of the alkyl unit, and a triplet ($J = 7.84$ Hz) at δ 1.95 for the CH_2 protons attached to C-9 of the fluorene moiety. The *O*-methylene protons appeared as a singlet at δ 5.30 in addition to the aromatic protons. In the ^{13}C NMR spectrum, the aliphatic carbons appeared at δ 14.3–40.5 and the methylene carbon attached at C-9 of the fluorene moiety and *O*-methylene carbons appeared at δ 54.8 and at δ 71.6, respectively, in addition to the aromatic carbons.

In order to test the utility of this synthetic process, precyclophanes **8a**, **9a**, **9b**, **10a**, and **10b** were synthesized by the reaction of 1.0 equiv of **7a–b** with 2.5 equiv of catechol, resorcinol and hydroquinone in 68%, 62%, 59%, 50%, and 58% yields, respectively. The structures of precyclophanes **8a**, **9a–b**, and **10a–b** were confirmed from spectroscopic and analytical data.[10,11] Precyclophanes **8a**, **9a–b**, and **10a–b** were next coupled with 1.0 equiv of **7a** or **7b** under high dilution conditions to give fluorenophanes **1a–3a** and **2b–3b** in 31%, 28%, 19%, 27%, and 16% yields, respectively (Scheme 1). The structures of fluorenophanes **1a–3a** and **2b–3b** were characterized by spectral and analytical data.[12,13]

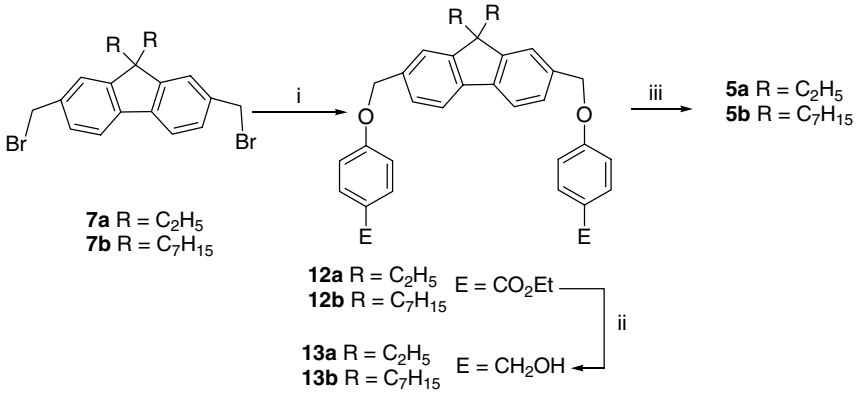
Using similar methodology, chiral precyclophanes **11a–b** were treated with **7a–b** to give chiral fluorenophanes **4a** and **4b** in 21% and 18% yields, respectively (Scheme 2). The structures of chiral fluorenophanes **4a** and **4b**[14] were confirmed from spectroscopic and analytical data.

The synthesis of a fluorenophane with a large cavity would be of interest. The treatment of 1.0 equiv of dibromide **7a–b** with 2.1 equiv of ethyl 4-hydroxybenzoate **6** in dry DMF in the presence of K_2CO_3 at 60 °C for 48 h afforded diesters **12a–b** in 82% and 87% yields. Reduction of diesters **12a–b** with LAH in THF gave diols **13a–b** in 68% and 71% yields. Dibromide **7a–b** was slowly added to a suspension of diol **13a–b** in excess NaH in dry THF over a period of 6 h to give fluorenophanes **5a–b** in 32% and 27% yields (Scheme 3). The structures of fluorenophanes **5a–b** were characterized by spectral and analytical data.[15]

Semi empirical energy minimization calculations using the MOPAC (AM1) method were carried out for the *syn* and *anti* isomers of fluorenophane **1a**. The heat of



Scheme 2. Reagents and conditions: (i) S-Binol, K_2CO_3, dry acetone, rt, 48 h, **11a** (58%), **11b** (62%); (ii) **7a/7b** K_2CO_3, dry acetone, high dilution condition, rt, 120 h, **4a** (21%), **4b** (18%).



Scheme 3. Reagents and conditions: (i) **6**, K_2CO_3, dry DMF, 60 °C, 48 h, **12a** (82%), **12b** (87%); (ii) LAH, THF, 60 °C, 12 h, **13a** (68%), **13b** (71%); (iii) **7a**/**7b** NaH, THF, 60 °C, 12 h, **5a** (32%), **5b** (27%).

formation of the *syn* isomer of **1a** is 8.165 kcal mol^{-1}, while that of the *anti* isomer is 8.901 kcal mol^{-1} (Figs. 1 and 2). Thus the *syn* isomer is more stable than the *anti* isomer and hence formation of the *syn* isomer is more favored than the *anti* isomer. The ^1H NMR spectrum of the *syn* isomer of **1a** shows a sharp singlet at δ 5.30 for the *O*-methylene protons. If the *anti* isomer of **1a** had been obtained there would have been two singlets and the chemical shifts of the *O*-methylene protons would also have been different.

All the fluorenophanes showed UV–vis absorption maxima at 301–310 nm. The photoluminescence emission spectra of the fluorenophanes show typical vibronically structured bands comprising a maximum, a shoulder and a tail at 400, 425, and 460 nm, 410, 420, and 450 nm, and 380, 430, and 460 nm, for **1a**, **1b**, and **4a**, respectively.

Dibromide **7a** shows weaker fluorescence when compared to **7b**. Because of the increasing alkyl chain length a slight increase in the emission was observed at 352 nm. The photoluminescence emission of fluorenophanes **1a**, **1b**, and **4a** exhibited red shifts (bathochromic shift) of about 68, 68, and 78 nm, respectively (Fig. 3).

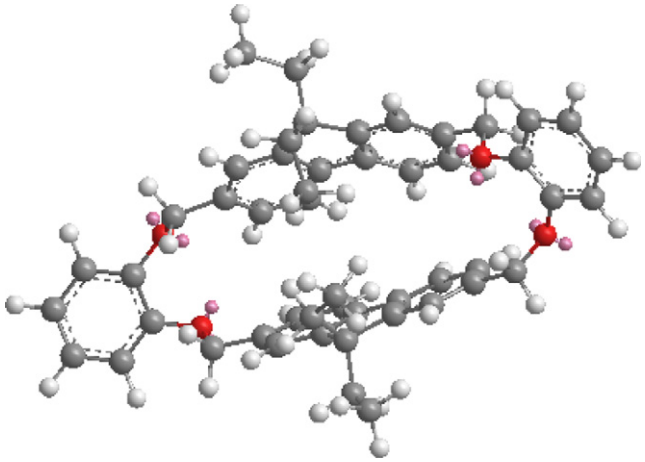


Figure 1. The heat of formation of the *syn* isomer of fluorenophane **1a** is 8.165 kcal mol^{-1}.

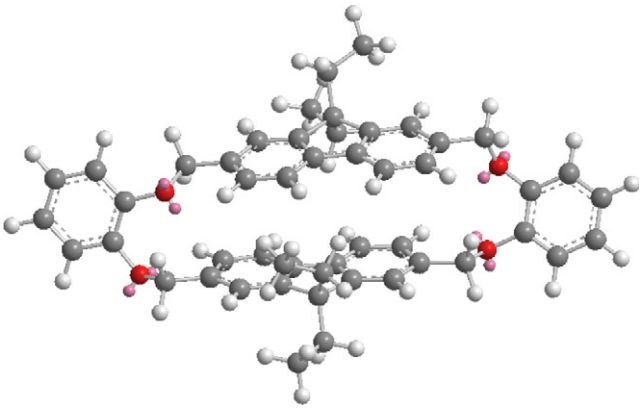


Figure 2. The heat of formation of the *anti* isomer of fluorenophane **1a** is 8.901 kcal mol^{-1}.

The results obtained in the present study reveal that the conformational properties of the 2,7-bridged fluorenophanes depend on the molecular structure, especially that of the polynuclear aromatic components as well as the length of the alkyl chain. The bathochromic shift of the fluorenophanes originated from transannular interactions between the two aromatic components. The fluorenophanes described herein exhibited a characteristic behavior that might be due to efficient energy

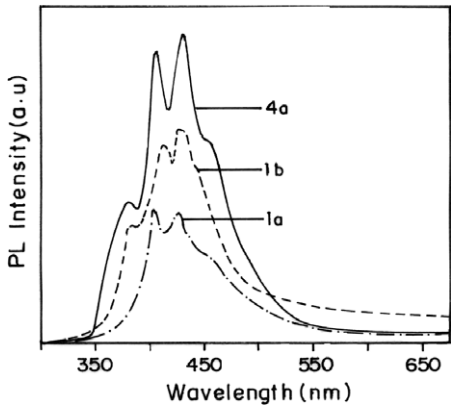


Figure 3. Photoluminescence spectrum of fluorenophanes **1a**, **1b**, and **4a**.

transfer from the fluorene moiety to the aromatic component.

Acknowledgements

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10. Precyclophane **10a**: Yield 50%; mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.32 (t, $J = 7.34$ Hz, 6H); 1.70 (q, $J = 7.32$ Hz, 4H); 4.75 (s, 4H); 6.43 (d, $J = 8.8$ Hz, 4H); 6.56 (d, $J = 8.8$ Hz, 4H); 7.01–7.38 (m, 6H); 8.36 (s, 2H, exchangeable with D_2O): ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.0, 71.4, 116.3, 119.6, 122.2, 122.8, 126.4, 126.7, 127.0, 135.9, 141.1, 152.9; Mass 466 (M^+ 466). Elemental Anal. Calcd for $C_{31}H_{30}O_4$: C, 79.83; H, 6.44. Found: C, 79.68; H, 6.37.
11. Precyclophane **10b**: Yield 58%; mp 111–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71 (t, $J = 7.1$ Hz, 6H); 1.06–1.18 (m, 20H); 1.84–1.88 (m, 4H); 5.00 (s, 4H); 6.67 (d, $J = 8.8$ Hz, 4H); 6.80 (d, $J = 8.8$ Hz, 4H); 7.23–7.61 (m, 6H); 8.24 (s, 2H, exchangeable with D_2O): ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 23.7, 28.6, 29.9, 31.7, 40.2, 54.9, 71.4, 119.6, 119.6, 122.8, 124.0, 126.2, 126.6, 127.0, 135.9, 140.9, 151.0; (QIP-MS) 606 (M^+ 606). Elemental Anal. Calcd for $C_{41}H_{50}O_4$: C, 81.18; H, 8.25. Found: C, 81.01; H, 8.18.
12. Cyclophane **3a**: Yield 19%; mp 132–137 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.31 (t, $J = 6.8$ Hz, 12H); 2.02 (q, $J = 6.1$ Hz, 8H); 5.07 (s, 8H); 6.93–7.32 (m, 12H); 7.69 (d, $J = 7.6$ Hz, 8H): ^{13}C NMR (100 MHz, $CDCl_3$): 8.6, 32.7, 52.0, 72.3, 101.4, 116.2, 119.9, 122.1, 123.4, 126.3, 126.9, 133.6, 139.2, 157.6; (QIP-MS) 712 (M^+ 712). Elemental Anal. Calcd for $C_{50}H_{48}O_4$: C, 84.26; H, 6.74. Found: C, 84.12; H, 6.60.
13. Cyclophane **3b**: Yield 16%; mp 102–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78 (t, $J = 11.2$ Hz, 12H); 1.04–1.26 (m, 40H); 1.96 (t, $J = 8.4$ Hz, 8H); 5.08 (s, 8H); 6.93–7.37 (m, 12H); 7.68 (d, $J = 7.6$ Hz, 8H); (QIP-MS) 992 (M^+ 992). Elemental Anal. Calcd for $C_{70}H_{88}O_4$: C, 84.67; H, 8.87. Found: C, 84.56; H, 8.97.
14. Chiral cyclophane **4b**: Yield 18%; mp 169–172 °C; $[\alpha]_D^{25}$ −118 (*c*, 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8 (t, $J = 7.32$ Hz, 12H); 0.92–1.24 (m, 40H); 1.84 (m, 8H); 5.15 (s, 8H); 6.92–8.09 (m, 36H): ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 23.7, 29.0, 30.9, 40.3, 54.9, 71.6, 116.0, 119.2, 119.6, 121.2, 122.8, 123.9, 126.5, 126.9, 127.0, 128.1, 129.4, 129.6, 134.3, 136.3, 140.9, 151.0; (QIP-MS) 1344 (M^+ 1344). Elemental Anal. Calcd for $C_{98}H_{104}O_4$: C, 86.43; H, 7.73. Found: C, 86.22; H, 7.51.
15. Cyclophane **5a**: Yield 32%; mp 152–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02 (t, $J = 7.2$ Hz, 12H); 1.70–1.74 (m, 8H); 4.19 (s, 8H); 4.46 (s, 4H); 6.94–7.43 (m, 20H): (QIP-MS) 740 (M^+ 740). Elemental Anal. Calcd for $C_{52}H_{52}O_4$: C, 84.32; H, 7.03. Found: C, 84.11; H, 6.93.