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Tetrahedron Letters 44 (2003) 8211–8215

TETRAHEDRON
LETTERS

Cavitands bearing four fluorophores

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Received 20 August 2003; revised 9 September 2003; accepted 11 September 2003

Abstract—The synthesis of novel cavitands containing four fluorophores [*tert*-butoxycarbonyl protected 2,2′-bis(furyl)benzidine (*t*-BOC FurylBz) or 5,5′-bis(4-aminophenyl)-2,2′-bifuryl (*t*-BOC PFDA)] and ionophoric functional groups on the upper rim is reported. The cavitands bearing the four fluorophores emit blue light photoluminescence. In particular, the cavitand containing PFDA moieties exhibits a high photoluminescence quantum yield.

Cavitands, molecules that contain a rigid enforced cavity, have attracted considerable attention in supramolecular chemistry as building blocks for the construction of carcerands, hemicarcerands, and other hosts.[1–6] On the other hand, luminescent organic molecules and their design and synthesis have recently become an important area of research for the development of molecular photonic devices such as light-emitting diodes[7–9] and optical sensors.[10–12] It is indeed an interesting research subject to meld molecular recognition and luminescent characteristics into one molecular system, producing a new type of supramolecule having dual functionalties as receptor and fluorophore.[13,14] We report here the synthesis of cavitands bearing four fluorophores (see an example shown in Figure 1), and their photoluminescent properties including quantum yields.

Syntheses of *tert*-butoxycarbonyl protected 5,5′-bis(4-aminophenyl)-2,2′-bifuryl (*t*-BOC PFDA) and 2,2′-bis(furyl)benzidine (*t*-BOC FurylBz) are based on the modification of a known procedure.[15,16] The desired cavitands having four fluorophores (**9**, **10**, and **11**) on the upper rim of cavitands (**1** and **2**) were prepared by using amide coupling as a key reaction (Scheme 1). In order to connect the upper rim of cavitands and fluorophores, we have used a spacer containing –$CH_2C(O)$–, which can play as complexing moieties for metal ions.[17,18] Treatment of **1** with four equivalents of $BrCH_2C(O)OEt$ gave tetraester **3**. Tetraester **3** was hydrolyzed under basic conditions to give tetraacid **5**[19] which, upon treatment with oxalyl chloride (20 equivalents) gave the corresponding tetraacyl chloride **7**. Compound **7** was isolated in essentially quantitative yield and used for next steps without further purification or characterization. Analogously, tetraol **2** was converted to the corresponding tetraacyl chloride **8** in high yield. The coupling of tetraacyl chloride **7** with *t*-BOC protected FurylBz was performed in CH_2Cl_2 using Et_3N as a base to give TetraFurylBz **9** in 48% yield. TetraFurylBz **10** was also prepared in 35% yield from tetraacyl chloride **8** under the similar conditions. Treatment of *t*-BOC protected PFDA with tetraacyl chloride **7** likewise provided TetraPFDA **11** in 56% yield. The products were identified by infrared (IR), proton and carbon nuclear magnetic resonance (^1H and ^{13}C NMR), and mass spectroscopy.[20]

The photoluminescent properties of the fluorophores and the fluorescent cavitands **9**, **10** and **11** were investigated. Photoluminescence (PL) spectra were measured at room temperature using a fluorescence spectrophotometer (PTI Fluorescence System) with a Xenon Lamp. For both excitation and emission monochromators, band-passes were 2 nm, respectively. The PL behavior

Keywords: cavitands; fluorophores; absorption; photoluminescence; blue light emit; quantum yield; receptor; dual functionalities.

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doi:10.1016/j.tetlet.2003.09.070

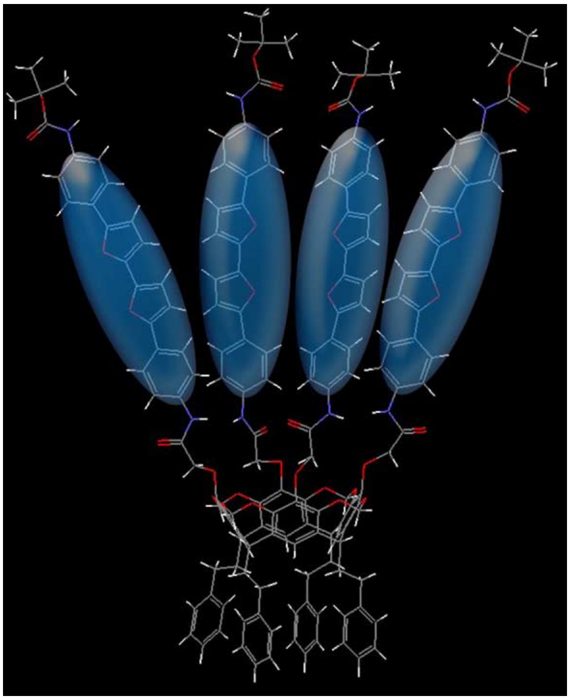
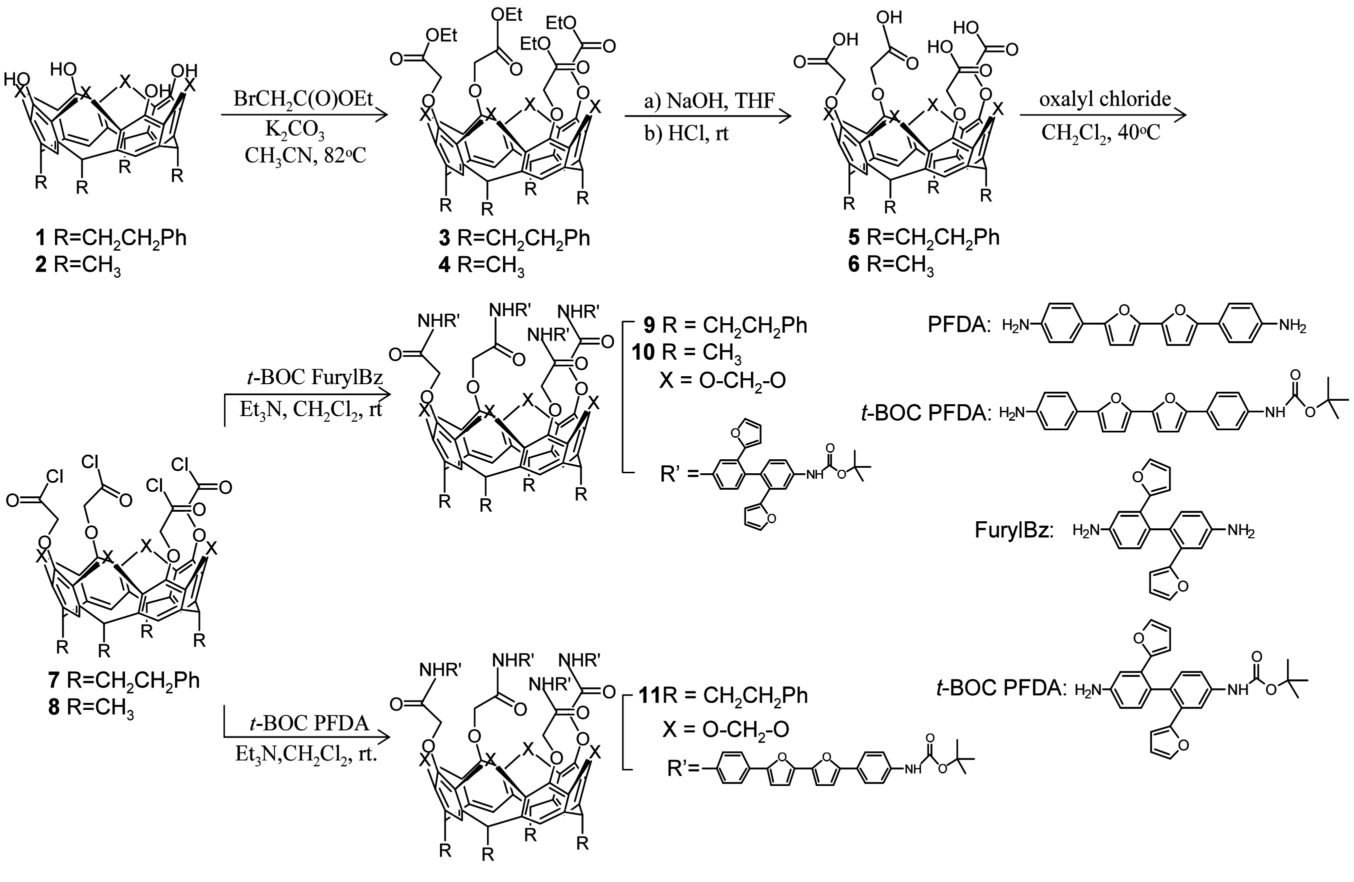


Figure 1. Molecular structure of a cavitand bearing four fluorophores (TetraPFDA **11**); the blue colored ellipsoids indicate four fluorophore bulbs emitting blue light. The atoms are distinguished as O, red; C, grey; N, blue.

of the samples was investigated for their solutions with a concentration of 1.5×10^{-5} g/mL in 1,4-dioxane. The obtained UV-vis absorption (Abs) and PL spectra are shown in Figure 2 and 3. FurylBz in 1,4-dioxane has an absorption maximum at 328 nm which is considered to be the π–π* transition, leading to the formation of a singlet exciton. With this UV-vis absorbance characteristic, the solution of FurylBz was excited at a wavelength of 328 nm, exhibiting a PL emission peak at 434 nm. In addition, PFDA exhibited a broad featureless absorption with its low energy edge lying at ca. 376 nm. PFDA exhibited two emission peaks at 415 and 440 nm when excited at a wavelength of 380 nm. Both fluorophores emit a very intense blue fluorescence.

On the other hand, TetraFurylBz **9** and TetraFurylBz **10** had absorption peaks at 258 and 256 nm, respectively. When TetraFurylBz **9** in the solution was excited at 288 nm, it had the best fluorescence spectrum with respect to intensity. TetraFurylBZ **9** showed a peak maximum at 404 nm in the emission spectrum, which was substantially blue-shifted in comparison to FurylBz with a PL peak at 434 nm. Similarly, TetraFurylBz **10** was excited at 287 nm, which provided the best fluorescence spectrum with respect to intensity. It had a PL peak maximum at 405 nm.

Here, one can see two peculiar phenomena for TetraFurylBz **9** and **10**. First, the absorption at ca. 328 nm due to the π–π* transition is decreased, compared to



Scheme 1.

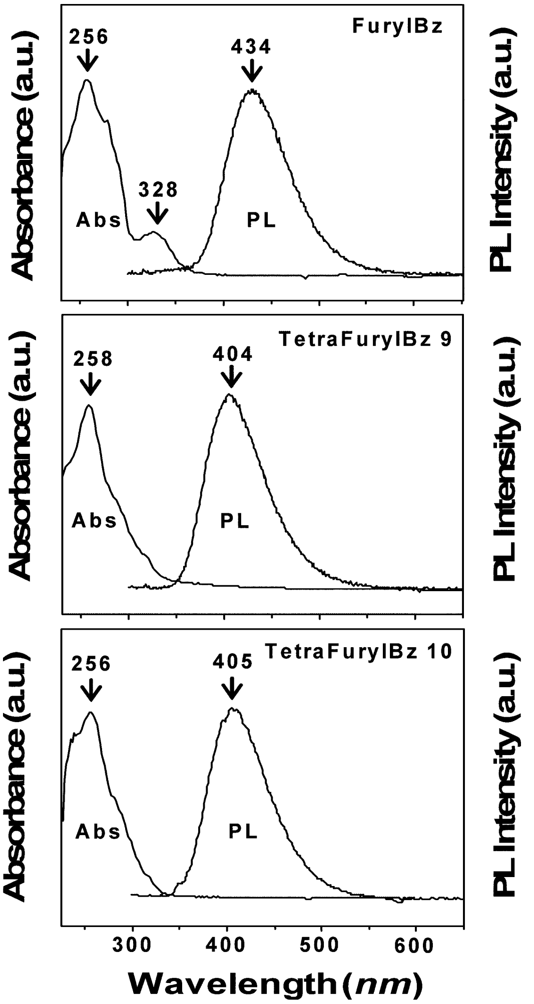


Figure 2. UV-Visible absorption (Abs) and photoluminescence (PL) spectra of FurylBz and TetraFurylBz **9**, **10**.

that of FurylBz. Second, the PL peaks are blue-shifted. We believe that these phenomena are attributed to the effect of molecular conformations on the ground-state and excited-state electronic structures of the FurylBz attached to the upper rim of cavitands. FurylBz has two furyl side groups, so that it is bulky by itself. If four *t*-BOC protected FurylBz molecules are coupled with a cavitand, they have more steric hindrance and their structures are twisted on the upper rim of the cavitand. Thus, one can expect a large change in the molecular conformation of the protected FurylBz on the upper rim of the cavitands and its electronic structure with shortened conjugation length, compared to those of FurylBz. In addition, the *t*-BOC group substituted on FurylBz may affect the conformational and/or electronic structure of **9** and **10**. However, TetraPFDA **11** having the same *t*-BOC group reveals the Abs and PL peaks which resemble those of PFDA as seen in Fig. 3; in the case of **11**, the effect of *t*-BOC group on the Abs and PL peaks is negligible. Taking this fact into account, the effect of *t*-BOC group on the Abs and PL peaks of **9** and **10** is expected to be negligible. Consequently, the change of the electronic structure due to the conformational modification of FurylBz induces such weakening in the absorption at 328 nm and such blue-shift in the PL peaks for TetraFurylBz **9** and **10**.

TetraPFDA **11** solution had an absorption peak at 378 nm and two PL peaks at 413 and 437 nm which were excited at 377 nm. The absorption and PL spectra of TetraPFDA **11** are very similar to those of PFDA. There is only a little shifting of absorption and PL peaks in the case of TetraPFDA **11**. This observation might be understood as follows. PFDA has furyl groups between two phenyl rings, so it is less bulky than FurylBz. Accordingly, when four *t*-BOC protected PFDA molecules are connected to the upper rim of a cavitand, the steric hindrance is relatively small and thus the conformational change in the structure of PFDA is little, compared to those of FurylBz. Consequently, there is only a little change of the electronic structure of PFDA due to the coupling with **7**, so that the absorption and PL peaks of TetraPFDA **11** remain nearly unchanged, compared to those of PFDA.

We also measured the PL quantum yields of the fluorescent cavitands. Relative PL quantum yield was determined by comparing the ratio of the fluorescence emission intensity maximum to UV-vis absorbance at excitation wavelength used for a sample with that of a standard. Absorbances of all sample solutions were kept between 0.05 and 0.08 by changing concentrations, in order to avoid any inner filter effect. Here, quinine sulfate was employed as a standard: quinine sulfate in 1.0 N H_2SO_4 at 23±1°C was reported to have $\Phi_f = 0.55$ when excited at 365 nm.[21–24]

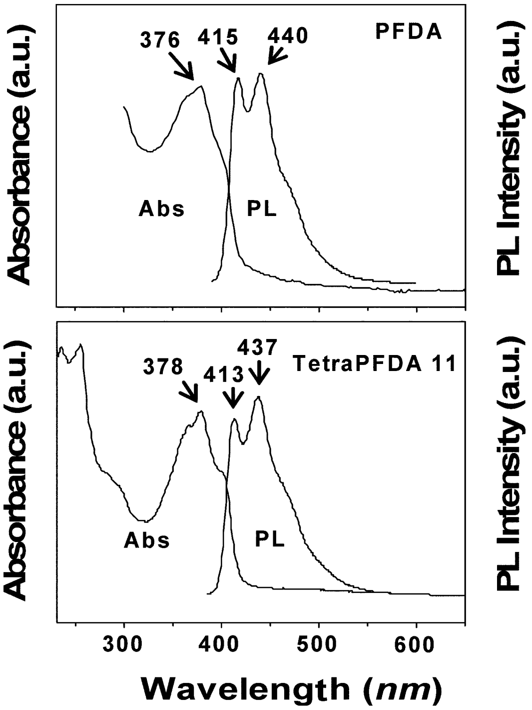


Figure 3. UV-Visible absorption (Abs) and photoluminescence (PL) spectra of PFDA and TetraPFDA **11**.

Table 1. Quantum yields of the flourophores and the fluorescent cavitands

Compounds	PFDA	FurylBz	**9**	**10**	**11**
Φ_f	0.92	0.52	0.09	0.06	0.73

Refractive indices of pure 1.0 N H_2SO_4 and 1,4-dioxane were used for the standard and the sample solutions in the estimation of quantum yield. Quantum yields reported here were averaged over at least three measurements, with a standard deviation below 0.03 (Table 1). PL quantum yields of FurylBz and PFDA are measured to be 0.52 and 0.92, respectively. In the case of PFDA, its quantum yield is relatively very high. For TetraFurylBz **9** and **10**, relative quantum yields were 0.09 and 0.06, respectively. They have lower PL efficiencies than FurylBz. The quantum yield of Tetra-PFDA **11** was 0.73, which is also lower than that of PFDA. In comparison, the quantum yield of Tetra-PFDA **11**, however, is much higher than those of TetraFurylBz **9** and TetraFurylBz **10**.

Overall, cavitands bearing four fluorophores have a lower PL quantum yield compared to that of the corresponding fluorophore itself. These results might be due to two major factors as follows. The first contributing factor may be an increase in the interaction between four fluorophores attached to the upper rim of cavitands that can affect nonradiative decay processes of the excited states, in comparison to fluorophore itself which is not attached onto cavitand. The second factor may be an unfavorable conformational change of the fluorophores via their attachment to the cavitands, which can shorten their π-conjugation length, consequently lowering quantum yield in the photoluminescence.

In conclusion, we have demonstrated the synthesis and photoluminescent properties of fluorophores and cavitands with four fluorophores on their upper rim. These new fluorescent cavitands **9**, **10** and **11** have not only fluorophores which can emit photoluminescence but also ionophoric functional groups such as amide linkages attached to their phenolic oxygen atoms that can act as complexing moieties for metal ions and organic cations. In particular, the cavitand **11** exhibits a high quantum yield in the photoluminescence. Therefore, these cavitands have potential applications in optical and chemical sensors. In addition, these are useful as intermediate compounds for synthesizing a variety of new functional cavitands since each fluorophore moiety owns a reactive amino group at the end after the *t*-BOC groups are deprotected.

Acknowledgements

This study was supported by the Center for Integrated Molecular Systems (KOSEF) and by the Ministry of Education (BK21 Program).

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20. Selected data for **9**: m.p. >246°C dec.; ^{1}H NMR (δ, DMSO-d_6): 9.96 (s, 1H, CH$_2$C(O)N*H*), 9.57 (s, 1H, OC(O)N*H*), 7.61 (d, 1H, Ph-*H*), 7.54 (s, 2H, fuyl-*H*), 7.44 (s, 1H, Ph-*H*), 7.40 (d, 1H, Ph-*H*), 7.20 (br s, 5H, Ph-*H*), 7.10 (d, 1H, Ph-*H*), 7.01 (d, 1H, Ph-*H*), 6.22 (d, 2H, furyl-*H*), 6.05 (d, outer of OC*H*$_2$O), 5.30 (s, 2H, furyl-*H*), 4.69 (br s, 3H, CH$_2$CH$_2$C*H*, OC*H*$_2$C(O)), 4.52 (d, 1H, inner of OC*H*$_2$O), 2.63 (br s, 4H, CHC*H*$_2$C*H*$_2$), 1.51 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (δ, DMSO-d_6): 166.92, 152.73, 151.47, 151.21, 146.52, 143.60, 142.14, 142.03, 141.41, 139.37, 138.82, 137.82, 133.05, 131.22, 131.10, 130.76, 129.49, 129.19, 128.36, 128.19, 125.79, 118.53, 117.35, 116.29, 115.70, 114.92, 111.61, 111.47, 108.33, 108.08, 99.50, 79.17, 72.10, 36.88, 33.74, 31.34, 28.07; IR (KBr, cm^{-1}): 3336, 2976, 2934, 1693, 1609, 1585, 1524, 1494, 1478, 1390, 1368, 1315, 1235, 1157, 1050, 1018, 973, 738, 701; *m*/*z* (FAB, NBA) 2842.19 [M+H]$^+$. For **10**: m.p. >267°C dec.; ^{1}H NMR (δ, DMSO-d_6): 9.97 (s, 1H, CH$_2$C(O)N*H*), 9.61 (s, 1H, OC(O)N*H*), 8.24 (s, 1H, Ph-*H*), 8.14 (s, 1H, Ph-*H*), 7.65–7.58 (m, 4H, Ph-*H*, furyl-*H*), 7.43 (d, 1H, Ph-*H*), 7.12 (d, 1H, Ph-*H*), 7.03 (d, 1H, Ph-*H*), 6.26 (m, 2H, furyl-*H*), 6.05 (d, 1H, outer of OC*H*$_2$O), 5.32 (d, 2H, furyl-*H*), 4.88 (d, 1H, CH$_3$C*H*), 4.70 (s, 2H, OC*H*$_2$C(O)), 4.50 (d, 1H, inner of OC*H*$_2$O), 1.88 (d, 3H, C*H*$_3$CH), 1.55 (s, 9H, C(C*H*$_3$)$_3$); IR (KBr, cm^{-1}): 3342, 2976, 2936, 1707, 1609, 1585, 1524, 1494, 1479, 1446, 1391, 1369, 1314, 1238, 1158, 1115, 1052, 1019, 982, 738; *m*/*z* (FAB, NBA) 2481.47 [M+H]$^+$. For **11**: m.p. >210°C dec.; ^{1}H NMR (δ, DMSO-d_6): 9.91 (s,

1H, $\mathrm{CH_2C(O)N}H$), 9.50 (s, 1H, $\mathrm{OC(O)N}H$), 7.75 (s, 4H, Ph-*H*), 7.67 (d, 2H, Ph-*H*), 7.54 (d, 2H, Ph-*H*), 7.43 (s, 1H, Ph-*H*), 7.20 (br s, 5H, Ph-*H*), 6.97 (d, 1H, furyl-*H*), 6.93 (d, 1H, furyl-*H*), 6.84 (d, 2H, furyl-*H*), 5.95 (d, 1H, outer of $\mathrm{OC}H_2\mathrm{O}$), 4.67 (br s, 3H, $\mathrm{CH_2CH_2C}H$, $\mathrm{OC}H_2\mathrm{C(O)}$), 4.49 (d, 1H, inner of $\mathrm{OC}H_2\mathrm{O}$), 2.62 (br s, 4H, $\mathrm{CHC}H_2\mathrm{C}H_2$), 1.49 (s, 9H, $\mathrm{C(C}H_3)_3$); IR (KBr, cm^{-1}): 3338, 2933, 1694, 1596, 1515, 1467, 1413, 1367, 1316, 1233, 1158, 1108, 1052, 1018, 972, 835, 779, 701; *m*/*z* (FAB, NBA) 2841.90 $[\mathrm{M+H}]^+$.

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