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Functionalization of aminocrown ethers with [2*H*]-chromene units by Buchwald–Hartwig C–N coupling for constructing of photoswitchable molecular devices

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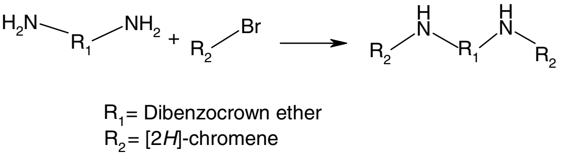
Abstract—Functionalization of the diaminodibenzocrown ethers with 2*H*-[1]benzopyrane and 3*H*-naphtho[2,1-*b*]pyrane units by Buchwald–Hartwig C–N coupling was developed. It is demonstrated that the novel molecule possesses photochromic properties that can be modified by the complex formation process.

Since Pedersen's discovery of the ability of crown ethers to complex alkali metal ions,[1] an amazing number of synthetic receptors for recognition of various guests have been prepared.[2] The development of novel molecular devices have attracted increasing attention for its application in miniaturized computer processors.[3] Functionalization of crown ethers with photochromic compounds enables to create optical switches with the photoreactivity in the absence and presence of guest substrates.[4]

One of the important criteria for selection of the signalling part is a visual color change. 2*H*-[1]Benzopyrane and naphtho[2,1-*b*]pyrane derivatives have been shown to possess photochromic properties.[5] Under UV light irradiation the colourless naphtho[2,1-*b*]pyrane form isomerizes to the colored merocyanine forms. The other high criterion for the creating of photosensible switches is an availability of the π-conjugated system over the whole molecule. In this case the addition of guests into the crown cavity could have a strong influence for the photochromic units.

Recently, the palladium-catalyzed amination of aryl halides by Buchwald–Hartwig C–N coupling has been developed as a convenient and useful synthetic method.[6] This approach may be useful for the synthesis of crowned naphthopyrans. Using this method we attempted to develop a macrocyclic system based on diaminodibenzocrown ether carrying two [2*H*]-chromene units (see Scheme 1).

In the first experiment, we used the reaction conditions previously described by Wolfe and Buchwald.[7] The compound **1** (see Scheme 2) was obtained by coupling reaction of 4-nitroaniline and 6-bromo-5,8-dimethyl-2,2-diphenyl-2*H*-chromene[8] in the presence of 2 mol % of palladium(II) acetate, 5 mol% of BINAP, 1.5 equiv of sodium *tert*-butoxide, 1.2 equiv of amine and 1.0 mmol of aryl bromide in toluene (1 mL/mmol) at 80 °C for 20 h in 67% yield.[9] Using this protocol, compound **2** was obtained in 12% yield from 1.4 mmol of-*cis*-4,4′-diaminodibenzocrown ether and 2.0 mmol 6-bromo-5,8-dimethyl-2,2-diphenyl-2*H*-chromene. However, a significant amount of starting material remained



Scheme 1.

Keywords: Naphtho[2,1-*b*]pyrane; 2*H*-[1]Benzopyrane; [2*H*]-Chromene; Diaminodibenzocrown ether; Buchwald–Hartwig C–N coupling; Photoswitchable devices.

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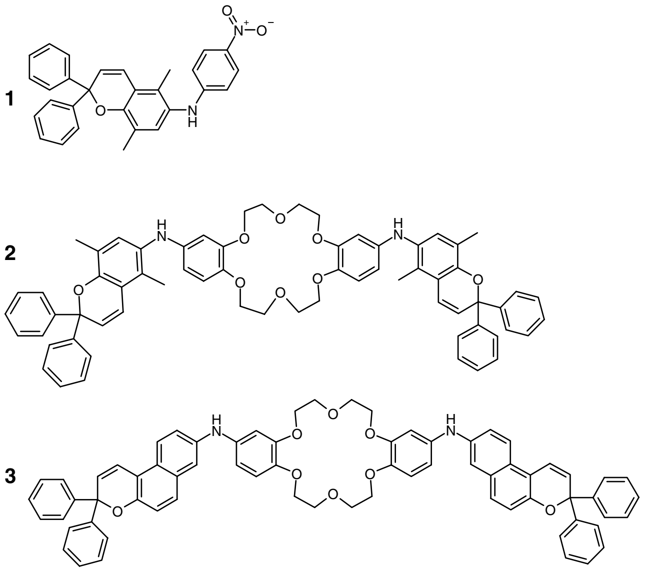

Scheme 2.

after 20 h of heating. Such a low yield could be explained by the influence of electron-donating oxygens to the amine in *cis*-4,4′-diaminodibenzocrown ether, while there was the electron-accepting nitro group in the 4-nitroaniline. We found that coupling in refluxing toluene in the presence of 1 mol % of tris(dibenzylideneacetone)dipalladium(0), 4 mol % of 2-(di-*t*-butylphosphino)biphenyl, 1.4 equiv of sodium *tert*-butoxide, 1.3 equiv of *cis*-4,4′-diaminodibenzocrown ether and 2.0 mmol of 6-bromo-5,8-dimethyl-2,2-diphenyl-2*H*-chromene gave compound **2** in 76% yield.[10] In a likewise fashion compound **3** was obtained from *cis*-4,4′-diaminodibenzocrown ether and 8-bromo-3,3-diphenyl-3*H*-benzo[*f*]chromene[11] in 69% yield.[12]

Photochemical properties of novel compounds were investigated. Maximum absorption wavelength for the compound **2** ($C = 2.5 \times 10^{-5}$ M) in acetonitrile under the dark conditions was observed at 265 nm. After the irradiation of UV light during 10 s the absorbance of closed form of crowned naphthopyrane decreased, while a new absorption peak was found at 588 nm indicating that the naphthopyrane moiety isomerized to its corresponding merocyanine forms.[5]

We further studied the binding properties of the compound **2**. Addition of tenfold excess of Na^+ to a solution of **2** ($C = 2.5 \times 10^{-5}$ M) in acetonitrile induced changes in the spectra. Photochemical behaviour of **2**–Na^+ was similar to that in the absence of cation, but the increase in absorbance (60% more) and broadening of the spectra signal of the open form were seen. These results suggest that the optical properties of compound **2** under light exposure could be modified by the complexation of the crown ether moiety, the enhancement of spectra signal might be due to the additional ionic interaction into the molecule.

Thus, in the present study, we developed functionalization of the diaminocrown ethers with 2*H*-[1]benzopyrane and naphtho[2,1-*b*]pyrane units by Buchwald–Hartwig C–N coupling. It is demonstrated that the obtained novel molecule possesses photochromic properties, which can be modified by the complex formation process. Since it is straight forward to synthesize this crowned naphthopyran derivative, it should be possible to prepare a wide range of useful photoswitchable devices. Further development of new compounds and studies of the mechanism of photoswitching are in progress.

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9. (5,8-Dimethyl-2,2-diphenyl-2*H*-chromen-6-yl)-(4-nitrophenyl)-amine **1**. A Schlenk flask was charged with aryl halide, amine, sodium *tert*-butoxide, palladium(II) acetate, BINAP and toluene under argon. The flask was immersed in an 80 °C oil bath with stirring until the starting material had been completely consumed as judged by GC analysis. The solution was allowed then to cool to room temperature, taken up in either and filtered. The solution was concentrated to dryness under reduced pressure. The crude material was purified by column chromatography. ^1H NMR (acetone, ppm): $\delta = 2.16$ (s, 3H), 2.33 (s, 3H), 3.02 (s, 1H), 6.46 (d, $J = 10.11$, 2H), 6.66 (d, $J = 9.16$, 2H), 6.95–7.00 (m, 1H), 7.24–7.50 (m, 6H), 7.50 (d, $J = 7.10$, 4H), 7.84 (br s, 1H), 8.03 (d, $J = 9.17$, 2H). ^{13}C NMR (acetone, ppm): $\delta = 154.7$ (1C), 150.1 (1C), 146.5

(2C), 139.0 (1C), 131.9 (1C), 130.3 (1C), 130.2 (1C), 130.0 (1C), 129.24 (4C), 128.48 (2C), 127.6 (4C), 127.0 (2C); 125.1 (1C), 122.2 (1C), 121.8 (1C), 113.0 (2C), 82.6 (1C), 16.0 (1C), 13.4 (1C).

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11. *N*,*N*′-Bis-(5,8-dimethyl-2,2-diphenyl-2*H*-chromen-6-yl)-6,7,9,10,17,18,20,21-octahydro-*H*,*H*,*H*,*H*-5,8,11,16,19,22-hexaoxa-dibenzo[*a*,*j*]cyclooctadecene-2,14-diamine **2**. ^{1}H NMR (acetonitrile, ppm): $\delta = 2.12$ (s, 6H), 2.26 (s, 6H), 3.89 (m, 8H), 4.00–4.14 (m, 10H), 6.15 (dd, $J_1 = 2.4$, $J_2 = 8.7$, 2H), 6.40 (d, $J = 2.4$, 2H), 6.45 (d, $J = 10.1$, 2H), 6.73 (d, $J_1 = 8.7$, 2H), 6.85 (br s, 2H), 6.92–7.00 (m, 2H), 7.23–7.42 (m, 14H), 7.49–7.75 (m, 4H). ^{13}C NMR (acetonitrile, ppm): $\delta = 148.6$ (2C), 148.2 (2C), 147.1 (2C), 146.1 (4C), 142.2 (2C), 135.8 (2C), 129.8 (2C), 128.9 (8C), 128.1 (4C), 127.0 (8C), 125.7 (2C), 124.2 (2C); 122.63 (2C), 121.6 (2C), 112.5 (2C), 112.0 (2C), 107.2 (2C), 101.8 (2C), 81.5 (2C), 69.6 (4C), 67.64 (4C).
12. *N*,*N*′-Bis-(3,3-diphenyl-3*H*-benzo[*f*]chromen-8-yl)-6,7,9,10,17,18,20,21-octahydro-*H*,*H*,*H*,*H*-5,8,11,16,19,22-hexaoxa-dibenzo[*a*,*j*]cyclooctadecene-2,14-diamine **3**. A Schlenk flask was charged with aryl halide, amine, sodium *tert*-butoxide, tris(dibenzilideneacetone)dipalladium(0), 2-(di-*t*-butylphosphino)biphenyl and toluene under argon. The flask was immersed in an 80 °C oil bath with stirring until the starting material had been completely consumed as judged by GC analysis. The solution was allowed then to cool to room temperature, taken up in either and filtered. The solution was concentrated to dryness under reduced pressure. The crude material was purified by column chromatography. ^{1}H NMR (acetonitrile, ppm): $\delta = 3.77$ (s, 8H), 4.00 (s, 8H), 6.37 (d, $J = 9.8$, 2H), 6.48–6.55 (m, 2H), 6.65 (d, $J = 9.8$, 2H), 6.74–6.85 (m, 4H), 7.05 (d, $J = 8.7$, 2H), 7.20 (d, $J = 7.7$, 4H), 7.28–7.45 (m, 16H), 7.49–7.58 (m, 2H), 7.59–7.66 (m, 2H), 7.75–7.90 (m, 2H). ^{13}C NMR (acetonitrile, ppm): $\delta = 153.2$ (2C), 151.5 (2C), 147.6 (2C), 147.3 (2C), 145.5 (2C), 143.7 (4C), 133.1 (2C), 130.8 (4C), 130.5 (4C), 129.3 (8C), 128.8 (2C), 128.7 (4C), 126.4 (2C), 125.2 (2C); 124.47 (2C), 124.0 (2C), 120.3 (2C), 116.6 (2C), 114.2 (2C), 112.6 (2C), 111.9 (2C), 106.5 (2C), 83.8 (2C), 71.0 (4C), 67.0 (4C).