Supporting Information

Isobenzotriazolophanes: A new class of fluorescent cyclophanes as sensors for aromatic nitro explosives - picric acid

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ES1 General experimental procedures of compound 1(a,b), 2(a,b) and 3(a,b).
ES2 1H NMR spectrum of 2-dodecyl benzotriazole
ES3 13CNMR spectrum of 2-dodecyl benzotriazole.
ES4 1H NMR spectrum of 4b.
ES5 13CNMR spectrum of 4b.
ES6 1H NMR spectrum of 5b.
ES7 13CNMR spectrum of 5b.
ES8 1H NMR spectrum of 6b.
ES9 13CNMR spectrum of 6b.
ES10 1H NMR spectrum of 1b.
ES11 13CNMR spectrum of 1b.
ES12 1H NMR spectrum of 7a.
ES13 13CNMR spectrum of 7a.
ES14 1H NMR spectrum of 8a.
ES15 13CNMR spectrum of 8a.
ES16 1H NMR spectrum of 2a.
ES17 13CNMR spectrum of 2a.
ES18 1H NMR spectrum of 8b.
ES19 13CNMR spectrum of 8b.
ES20 1H NMR spectrum of 2b.
ES21 13CNMR spectrum of 2b.
ES22 1H NMR spectrum of 9b.
ES23 13CNMR spectrum of 9b.
ES24 1H NMR spectrum of 10b.
ES25 13CNMR spectrum of 10b.
ES26  $^1$H NMR spectrum of 3b.
ES27  $^{13}$CNMR spectrum of 3b.
ES28  Mass spectrum of compound 3b.
ES29  Materials and Methods.
ES30  UV-VIS electronic absorption spectra of stilbenocarbazolophane 3b (A) and PA (B) in cyclohexane.
ES31  Emission spectra of stilbenocarbazolophane 3b (1 μM) in the absence and presence of the PA (1 mM) in cyclohexane.
ES32  UV-VIS electronic absorption (A) and fluorescence emission (B) spectra of Stilbenocarbazolophane 3b (5 μM) in cyclohexane [$\lambda_{ex} = 380$ nm and $\lambda_{em} = 450$ nm]
ES33  UV-VIS electronic spectra of PA (1 mM) in cyclohexane.
ES34  (A) UV-VIS electronic absorption (B) fluorescence emission spectra of Stilbenocarbazolophane 3b (5 μM) in cyclohexane in the presence of different concentration (100 μM - 800 μM) of PA.
ES35  A calibration plot, fluorescence intensity of Stilbenocarbazolophane 3b – PA against the concentration of PA in cyclohexane. [$\lambda_{ex} = 405$ nm & $\lambda_{ex} = 450$ nm]
ES36  Stern-Volmer plot in response to PA.
ES37  Extent of fluorescence quenching of carbazoloisobenzotriazolophane 3b with nitro aromatics.

ES1

**General procedure for synthesis of precyclophane by $N$-arylation of pyrole/indole/carbazole**

To a mixture of Cul (2.26 mmol), K$_3$PO$_4$ (28.3 mmol), trans-1,2-diaminocyclohexane (4.53 mmol) and indole (11.20 mmol) in toluene (150 mL) were added aryl dibromide (5.66 mmol) under nitrogen atmosphere. The reaction mixture was refluxed at 110 °C for 24 h. After the reaction was completed, the solvent was removed under reduced pressure and the residue was extracted with CHCl$_3$ (3 x 100 mL), washed with water (2 x 100 mL), brine (150 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed and crude product was purified by column chromatography on silica gel using CHCl$_3$/Hexane (1:4, v/v) as eluent.

**General procedure for synthesis of pyrole/indole dialdehyde**

To a stirred solution of dimethylformamide (19.9 mmol) at 0 °C, added phosphorous oxychloride (5.0 mmol) drop wise under nitrogen atmosphere. Bis-indole (2.3 mmol) in dimethylformamide (5.9 mmol) was then added to the reaction mixture at 0 °C and raised the temperature to 10 °C. After the completion of addition, the reaction mixture was allow to attain room temperature and then stirred for additional one hour at 35 °C. The reaction was then
quenched by adding crushed ice (100 g) and further water (100 ml). Then the reaction mixture was then treated thrice with NaOH solution (1 M). The reaction mixture was heated after adding one portion of NaOH solution and the rest of the two portions were added later with stirring. The reaction mixture was then kept in refrigerator overnight. The precipitate obtained was collected by filtration and then dissolved in chloroform (2 x 100 mL). The organic layer was washed with water (100 mL) and then dried over Na₂SO₄, filtered and solvent was evaporated under reduced pressure to give the residue which was then chromatographed over SiO₂ using chloroform/methanol (99:1) as eluting solvent to give the corresponding dialdehyde.

**General procedure for synthesis of carbazole dialdehyde**

To DMF (61.7 mmol) at 0 °C, phosphorous oxychloride (61.7 mmol) was added drop wise under nitrogen atmosphere. The solution was allowed to warm to room temperature, and then bis-carbazole (3.1 mmol) and 1,2-dichloroethane (DCE) (40 mL) were added. The reaction mixture was heated at 90 °C and kept at that temperature for 2 days. It was poured into water and extracted with CHCl₃ (2 x 100 mL). The chloroform extract was washed with water (2 x 100 mL) and solvent was removed under reduced pressure. The residue was purified by column chromatography using CHCl₃ (100%) as an eluent to give corresponding dialdehyde as a colourless solid.

**General procedure for McMurray coupling (Procedure D)**

A solution of low valent titanium prepared form TiCl₄ (20 equiv.) with zinc (40 equiv.) and two drops of pyridine in dry THF (200 mL) under nitrogen atmosphere at 0 °C and was allowed to attain room temperature after 0.5 h and then refluxed for 1 h. Dialdehyde (1 equiv.) was added in one batch to the freshly prepared low valent titanium. After the addition was over the reaction mixture was refluxed overnight. The reaction mixture was then cooled and quenched with saturated K₂CO₃ solution (50 mL). The precipitated inorganic material was removed by filtration. The precipitate was thoroughly washed with THF (2 x 100 mL) for several times and the combined THF extract on evaporation under reduced pressure gave the residue, which was extracted with CHCl₃ (100 mL), washed with water (2 x 100 mL) brine (100 mL) and dried over anhydrous Na₂SO₄. Crude product obtained after evaporation of CHCl₃, was purified by column chromatography using CHCl₃/Hexane (1:4, v/v) as eluent.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of 2-dodecyl benzotriazole
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 2-dodecyl benzotriazole
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 4b
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 4b
$^{1}H$ NMR spectrum (300 MHz, CDCl$_3$) of compound 5b
ES7

$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 5b
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 6b
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 6b
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 1b
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 1b
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 7a
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 7a
\(^1\)H NMR spectrum (300 MHz, CDCl\(_3\)) of compound 8a
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 8a
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 2a
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 2a
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 8b
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 8b
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 2b
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 2b
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 9b
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 9b
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 10b
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 10b
$^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound 3b
$^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound 3b
MALDI-TOF Mass spectra of compound 3b

ES29

Materials and Methods:
Materials:
Picric acid (PA) was purchased from Sigma-Aldrich chemical and used as a fluorescence quencher. Samples were made in spectral grade solvent cyclohexane purchased from SRL co.

Instruments:
Fluorescence emission spectra of the samples were measured using Fluoromax-4 (Horiba Jobin Yvon) spectrofluorometer, with a xenon lamp of 150 W as excitation source. Excitation and emission monochromator bandpasses were kept at 2 nm. UV-VIS electronic absorption spectra measurements were carried out in a Jasco V-650 UV-Visible Spectrophotometer with a scan rate of 1000 nm s\(^{-1}\).

Sample preparation:
A stock solution of non-polar stilbenocarbazolophane 3b was made in cyclohexane (1 mM). The concentration of sensor molecule, stilbenocarbazolophane 3b was optimized using fluorescence spectroscopic technique as 5 µM to sense PA. PA of different concentrations (10\(^{-4}\) M, 2×10\(^{-4}\) M, 4×10\(^{-4}\) M, 5×10\(^{-4}\) M, 6×10\(^{-6}\) M, and 8×10\(^{-4}\) M) was also made in cyclohexane.

ES30

UV-VIS electronic absorption spectra of stilbenocarbazolophane 3b (A) and PA (B) in cyclohexane

ES31
Emission spectra of stilbenocarbazolophane 3b (1 μM) in the absence and presence of PA (1 mM) in cyclohexane
ES32 UV-VIS electronic absorption (A) and fluorescence emission (B) spectra of stilbenocarbazolophane 3b (5 µM) in cyclohexane [\( \lambda_{\text{ex}} = 380 \text{ nm} \) and \( \lambda_{\text{em}} = 450 \text{ nm} \)]
UV-VIS electronic spectra of PA (1 mM) in cyclohexane
ES34 (A) UV-VIS electronic absorption (B) fluorescence emission spectra of carbazoiso benzotriazolophane 3b (5 µM) in cyclohexane at different concentration (100 µM - 800 µM) of PA.
Equation $y = a + b$.

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Fluorescence Int. (a.u.)

[PA] M

A
ES35 A calibration plot, fluorescence intensity of Stilbenocarbazolophane 3b – PA against the concentration of PA in cyclohexane. [$\lambda_{ex} = 405$ nm & $\lambda_{ex} = 450$ nm]
ES36 Stern-Volmer plot in response to PA

ES37 Extent of fluorescence quenching of carbazoloisobenzotriazolophane 3b (1 µM) observed at excitation wavelength [λ_ex = 405 nm] after the addition of 1mM of nitroaromatic compound in cyclohexane.