#Supplementary material (ESI) for Organic & Biomolecular Chemistry

Facile synthesis of novel indolo[3,2-*b*]carbazole derivatives and a chromogenic-sensing 5,12-dihydroindolo[3,2-*b*]carbazole

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1. General Method

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 300 (300 MHz) or a Bruker AMX-400 (400 MHz) spectrometers. NMR samples were run in the indicated solvents and were referenced internally. Chemical shift values were quoted in ppm and coupling constants were quoted in Hz. Chemical shift multiplicities were reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad. Low-resolution mass spectra were recorded on a HEWLETT-PACKARD instrument (CI or EI) and a LCQ Advantage instrument (ESI). Melting points were determined using a Reichert-Jung Thermovar apparatus and were uncorrected. X-Ray crystallography data were collected on a SMART 6000 diffractometer with CCD detector using Cu–Ka radiation (λ = 1.54178 A˚). Commercially available reagents were used as received.

2. Synthesis of *tert*-butylated ICZ: general procedure.

To the solution of ICZ (2 mmol) in $CHCl_3$ (20mL), $ZnCl_2$ (10 mmol) was added at room temperature under N_2 atmosphere. The mixture was stirred at room temperature for 15 minutes and the *t*-BuCl (10 mmol) was added dropwise into the reaction solution. The reaction mixture was heated at 70^{o} C overnight under N_2 atmosphere. When the reaction solution was cooled down to room temperature, H_2O (20mL) was added and the solution was extracted with CH_2Cl_2 (3 x 30mL). The organic solution was combined and dried with anhydrous $MgSO_4$. After concentration, the crude compound was purified by silica gel chromatography or dispersed in ethyl acetate (5mL) and then filtered off and washed with cold ethyl acetate (5mL) to give pure product.

Compound 4a: The crude product was purified by silica gel chromatography with EtOAc:Heptane (5:95) to give compound **4a** (0.85g, 77%) as a light yellow solid. Mp: >300ºC; $\lambda_{max}(CH_2Cl_2)$/nm 267 (ε/dm^{3}mol^{-1}cm^{-1} 40094), 279 (41512), 336 (58352), 377 (6578), 396 (6628); ν_{max}/cm^{-1} 3501 (NH), 2959, 2866, 1584, 1524, 1481, 1428;

δ_H(300MHz; $CDCl_3$; Me_4Si) 0.90 (3H, t, CH_3), 1.46–1.48 (20H, m, 6 x CH_3, 1 x CH_2), 1.62–1.63 (20H, m, 6 x CH_3, 1 x CH_2), 1.98–2.03 (2H, m, 1 x CH_2), 3.48 (2H, m, 1xCH_2) 7.45 (2H, S, 2 x CH), 7.8 (1H, s, 1 x CH), 8.00 (3H, s, 2 x CH, 1 x NH), 8.12 (1H, s, 1 x NH); δ_c(75MHz; $CDCl_3$; Me_4Si) 14.6 (CH_3), 23.3 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 30.8 (CH_3), 32.5 (CH_3), 33.1, 35.3, 98.1 (CH), 114.7 (CH), 117.1 (CH), 118.2, 120.3 (CH), 121.0 (CH), 123.5, 124.8, 131.9, 132.3, 135.0, 136.9, 142.1, 142.5; *m/z* (CI) 551 $[M+H]^+$.

Compound 4b: The crude compound was dispersed in ethyl acetate (5mL) and then filtered off and washed with cold ethyl acetate (5mL). After drying *in vacuo*, we got compound **4b** (0.59g, 47%) as a light yellow solid. Mp: >300ºC; λ_{max}(CH_2Cl_2)/nm 258 (ε/$dm^3mol^{-1}cm^{-1}$ 51305), 340 (42193), 405 (11716); ν_{max}/cm^{-1} 3493 (NH), 2953, 2903, 1867, 1583, 1541, 1483; δ_H(300MHz; $CDCl_3$; Me_4Si) 1.20 (18H, s, 6 x CH_3), 1.46 (18H, s, 6 x CH_3), 7.28 (2H, s, 2 x CH), 7.34 (2H, s, 2 x CH), 7.59–7.62 (2H, m, 2 x CH), 7.69 (4H, t, 4 x CH), 7.76 (4H, t, 4 x CH), 7.88 (2H, s, 2 x NH); δ_c(75MHz; $CDCl_3$; Me_4Si) 30.2, 31.7, 34.6, 34.7, 116.5, 116.6, 120.0, 120.2, 123.7, 128.0, 129.0, 129.2, 130.1, 131.1, 131.4, 134.1, 136.5, 137.2, 141.0; *m/z* (ESI) 633 $[M+H]^+$.

Compound 4c: This compound was prepared according to the general procedure using 6,12-bis(3,5-di-*tert*-butylphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (0.5g, 0.8mmol), $ZnCl_2$ (1.07g, 8mmol) and *t*-BuCl (1.35g, 8 mmol). The crude compound was dispersed in ethyl acetate (5mL) and then filtered off and washed with cold ethyl acetate (5mL). After drying *in vacuo*, we got compound **7c** (0.45g, 66%) as a yellow solid. Mp: >300ºC; λ_{max}(CH_2Cl_2)/nm 256 (ε/$dm^3mol^{-1}cm^{-1}$ 47137), 337 (46505), 404 (11711); ν_{max}/cm^{-1} 3494 (NH), 2965, 2905, 2868, 1593, 1538, 1480; δ_H(300MHz; $CDCl_3$; Me_4Si) 1.18 (18H, s, 6 x CH_3), 1.40 (54H, s, 18 x CH_3), 7.32 (2H, s, 2 x CH), 7.54 (6H, s, 6 x Ph-H), 7.62 (2H, s, 2 x CH), 7.78 (2H, br, 2 x NH); δ_c(300MHz; $CDCl_3$; Me_4Si) 30.6, 32.1, 32.2, 34.5, 116.9, 118.0, 120.4, 122.0, 124.2, 124.5, 131.5, 134.8, 136.8, 141.3, 152.2; *m/z* (ESI) 857 $[M+H]^+$.

3. Synthesis of 2,4,8,10-tetra-*tert*-butyl-6,12-diphenylindolo[3,2-*b*]carbazole (5b). To the solution of compound **4b** (80mg, 0.13mmol) in dry THF (10mL), *t*-BuLi (1.5M, 0.34mL, 0.52mmol) was added dropwise at 0 ºC. The reaction solution was stirred at room temperature for 4 hours. After the addition of H_2O (20mL), the solution was extracted with CH_2Cl_2 (3 x 30mL). The organic solution was combined and dried with anhydrous $MgSO_4$. After concentration, the crude compound was purified by silica gel chromatography with EtOAc:Heptane (5:100) to give compound **5b** (0.058g, 73%) as a violet solid. Mp: >300ºC; $\lambda_{max}(CH_2Cl_2)$/nm 316 (ε/dm^{3}mol^{-1}cm^{-1} 44207), 551 (21289), 590 (19402); ν_{max}/cm^{-1} 2957, 2905, 2868, 1592, 1482; δ_H(300MHz; $CDCl_3$; Me_4Si) 1.07 (18H, s, 6 x CH_3), 1.32 (18H, s, 6 x CH_3), 6.61 (2H, s, 2 x CH), 6.93 (2H, s, 2 x CH), 7.47 (6H, s, 6 x CH), 7.56 (4H, s, 4 x CH); δ_c(75MHz; $CDCl_3$; Me_4Si) 31.1, 31.3, 119.4, 124.4, 128.0, 129.3, 130.4; *m/z* (ESI) 631 $[M+H]^+$.

4. Synthesis of 2,4,8,10-tetra-*tert*-butyl-6,12-bis(3,5-di-*tert*-butyl)indolo[3,2-*b*]carbazoles (**5c**). To the solution of compound **4c** (40mg, 0.047mmol) in dry THF (10mL), *t*-BuLi (1.5M, 0.12mL, 0.18mmol) was added dropwise at 0 ºC. The reaction solution was stirred at room temperature for 4 hours. After the addition of H_2O (20mL), the solution was extracted with CH_2Cl_2 (3 x 30mL). The organic solution was combined and dried with anhydrous $MgSO_4$. After concentration, the crude compound was purified by silica gel chromatography with CH_2Cl_2:Heptane (1:9) to give compound **5c** (0.024g, 60%) as a violet solid. Mp: >300ºC; $\lambda_{max}(CH_2Cl_2)$/nm 306 (ε/dm^{3}mol^{-1}cm^{-1} 41474), 547 (17961), 586 (16042); ν_{max}/cm^{-1} 2963, 2905, 2867, 1593, 1476; δ_H(300MHz; $CDCl_3$; Me_4Si) 1.05 (18H, s, 6 x CH_3), 1.32 –1.34 (54H, m, 18 x CH_3), 6.44 (2H, s, 2 x CH), 6.92 (2H, s, 2 x CH), 7.29 (4H, s, 4 x CH), 7.49 (2H, s, 2 x CH); δ_c(75MHz; $CDCl_3$; Me_4Si) 31.2, 31.4, 32.0, 119.0, 123.1, 123.8, 124.2, 131.6, 132.7, 136.2, 141.6, 145.1, 150.5, 151.3, 155.0, 165.5; *m/z* (ESI) 855 $[M+H]^+$.

5. Synthesis of 2,4,8,10-tetra-*tert*-butyl-5,12-dihydroindolo[3,2-*b*]carbazole 6: To the solution of compound **4b** (0.1g, 0.16mmol) in dry THF (20mL) *n*-BuLi (1.6M, 0.2mL, 0.32mmol) was added dropwise at -76 ºC in the dark. After 20 minutes, *n*-BuLi (1.6M, 0.1mL, 0.16mmol) was added dropwise into reaction solution at -76 ºC in the dark. After 20 minutes, H_2O (20mL) was added to stop the reaction. Then the solution was extracted with CH_2Cl_2 (3 x 30mL). The organic solution was combined and dried with anhydrous $MgSO_4$. After concentration, the crude compound was purified by silica gel chromatography with EtOAc:Heptane (5:100) to give compound **6** (0.07g, 64%) as an orange solid. Mp: >300ºC; $\lambda_{max}(CH_2Cl_2)$/nm 267 (ε/dm^{3}mol^{-1}cm^{-1} 23955), 481 (17897); ν_{max}/cm^{-1} 3501 (NH), 2959, 2866, 1524, 1481, 1428; δ_H(300MHz; $CDCl_3$; Me_4Si) 0.73 (3H, s, 1 x CH_3), 0.87–0.90 (2H, m, 1 x CH_2), 1.13 (9H, s, 3 x CH_3), 1.20–1.22 (2H, m, 1 x CH_2), 1.28 (9H, s, 3 x CH_3), 1.43 (9H, s, 3 x CH_3), 1.55 (9H, s, 3 x CH_3), 2.78 (1H, dt, *J* 4.0 and 12.0, 1 x CH_2CHH–C), 3.21 (1H, dt, *J* 3.7 and 12.0, 1 x CH_2CHH–C), 6.82 (1H, s, 1 x CH), 7.10–7.12 (1H, m, 1 x CH), 7.13 (2H, t, 2 x CH), 7.23–7.24 (2H, m, 2 x CH), 7.29 (1H, s, 1 x CH), 7.53–7.55 (2H, m, 2 x CH), 7.63–7.68 (5H, m, 5 x CH), 7.95 (1H, s, 1 x NH); δ_c(75MHz; $CDCl_3$; Me_4Si) 13.7, 23.0, 27.0, 30.5, 30.7, 31.5, 31.8, 34.7, 34.77, 34.8, 35.6, 42.1, 50.6, 100.0, 115.3, 116.7, 119.4, 122.2, 126.2, 127.7, 127.8, 129.3, 129.7, 132.8, 132.9, 133.8, 134.0, 137.7, 141.2, 143.0, 145.5, 145.8, 151.5, 174.8; *m/z* (ESI) 689 $[M+H]^+$.

5. Crystallographic data for compound 4a:[1]

The crystals of **4a**, grown by evaporation from dichloromethane/DMSO, belong to the triclinic space group P-1. The crystal selected for data collection was transparent and

[1] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-686527 and CCDC- 686528. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk

had an average size of 0.4x0.2x0.1mm. Phi and omega scans were collected onto a SMART 6000 CCD detector using CuKα radiation (λ = 1.54178 Å) and the crystal was cryo-cooled at 100K. Cell refinement and data reduction were carried out by the program SAINT on a total of 21872 reflections (4308 independent reflections, R_{int} = 7.70%). Data completeness is 98.7% up to a 2θ angle of 143.34°.

The structure was solved by direct methods and refined by full-matrix least squares on $|F^2|$ using the SHELXTL program package converging to a final R_1 = 7.93%, ωR_2 = 17.48 for 3888 reflections with $I_o > 2\sigma(I_o)$ and GOOF = 1.245. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions with temperature factors fixed at 1.2 times U_{eq} of the parent atoms and 1.5 times U_{eq} for methyl groups.

Data were corrected for Lorentz and polarization effects and an absorption correction (SADABS) was performed.

Disorder is observed since the non-symmetrical compound is situated onto an inversion point. As such the compound is present in two orientations, rotated 180° with respect to each other, with the alkane chain pointing up and down the indolo[3,2-b]carbazole ring. Three disordered DMSO molecules are present in the unit cell.

6. Crystallographic data for compound 5b:[1]

The crystals of **5b**, grown by evaporation from dichloromethane, belong to the triclinic space group P-1. A red block like crystal with approximate dimensions of 0.3x0.1x0.1 mm was selected for data collection using CuKα radiation (λ = 1.54178 Å) and phi and omega scans. Data were collected at a temperature of 100K on a SMART 6000 CCD detector. Cell refinement and data reduction were carried out by the program SAINT on a total of 11666 reflections (3444 independent reflections, R_{int} = 7.46%). Data completeness is 99.6% up to a 2θ angle of 135.4°. The structure was solved by direct methods and refined by full-matrix least squares on $|F^2|$ using the SHELXTL program package converging to a final R_1 = 5.77%, ωR_2 = 13.84 for 2507

reflections with $I_o > 2\sigma(I_o)$ and GOOF = 1.024. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions with temperature factors fixed at 1.2 times U_{eq} of the parent atoms and 1.5 times U_{eq} for methyl groups. The hydrogen atoms were able to ride on the parent atoms.

Data were corrected for Lorentz and polarization effects and a absorption correction (SADABS) was performed.

The compound is perfectly symmetrical and is situated onto an inversion point which generates the other half of the compound. The benzene ring makes an angle of 63.0° with the indolocarbazole group.