Oxidative reactions of 6-pentyl indolo[3,2-*b*]carbazole: formation of novel C–C and C–N coupled dimers

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The oxidative coupling reactions of 6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole have been studied and as a result, a number of novel dimers of the indolo[3,2-*b*]carbazole derivative have been prepared, forming C–C coupled compound **3** when treated with $FeCl_3\cdot6H_2O$ or C–N coupled compounds **4** and **5** when oxidized with air or $Pd(OAc)_2$, respectively.

Introduction

Over the past decade, electroactive molecules have been applied as active components in electronic devices such as light emitting diodes (LED),[1] field effect transistors (FETs),[2] and photovoltaic cells (PCs).[3] Indeed, organic materials are very attractive due to their good mechanical properties, low cost, and their tunable electrical and optical properties through structure modification.[4] However, stability and processability together with good charge transport properties are still important problems not yet solved. In 1999, Hu *et al.* reported the first indolo[3,2-*b*]carbazole derivative, 5,11-dihydro-5,11-di-1-naphthylindolo[3,2-*b*]carbazole, which shows an unusual atropisomerism and excellent hole-transport properties in organic LEDs.[5] In 2004, Wakim *et al.* successfully fabricated the first OFET (organic field-effect transistor) using 5,11-dioctyl-6,12-dimethylindolo[3,2-*b*]carbazole as an active layer.[6] Recently, it has been reported that *N*,*N*′-disubstituted indolo[3,2-*b*]carbazoles present a new class of high-performance p-channel semiconductors and can be used to fabricate high-mobility OTFTs (organic thin-film transistors).[7] Blouin *et al.* synthesized the new polyindolocarbazoles, polydiindolocarbazole and poly(indolo-carbazole-*alt*-bithiophene)s and their optical, electrochemical, magnetic and conductive properties have been studied.[8]

Although several synthetic pathways towards indolo[3,2-*b*]carbazole (ICZ) and its derivatives have been developed, most of the methods involve multi-step procedures starting from indole and afford the target ICZs in low overall yields. We previously reported an efficient three-stage one-pot procedure to synthesize the novel 6-monosubstituted 5,11-dihydroindolo[3,2-*b*]carbazoles.[9] The better solubility of these asymmetrical ICZs in apolar organic solvents allows for easier structural modifications.

In this paper, we demonstrate the synthesis of novel dimers of 6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole, through 12,12′ C–C or 12,11′ C–N bond, by oxidative coupling in moderate yields. To the best of our knowledge, this is the first report about the dimerization of ICZs and the examples of C–N dimers.

Results and discussion

Synthesis

It has been shown that chemical oxidation of *N*-alkylcarbazoles by anhydrous $FeCl_3$ exclusively yields dimers, which are linked at the 3,3′-positions (Fig. 1).[10] These compounds could be used as host materials for triplet emitters in organic light-emitting diodes,[11] hole-transporting glass-forming materials and could be used for hole transportation in orgainc semiconducting devices such as electroluminescence devices and solar cells.[10,12] According to the same method, we treated compound **1** with anhydrous $FeCl_3$ (Scheme 1(i)). However, we obtained mainly 12-chlorinated ICZ **2** in 50% yield together with a small amount (the yield is lower than 5%) of compound **3** (*m*/*z* 651 $[M + H]^+$). Detailed analysis of the NMR data confirmed that the latter compound **3** was indeed the dimer of compound **1**, with a C–C link at the 12,12′-positions. We repeated the reaction at different temperatures and with different amounts of reagents. We found that the small amounts of dimer **3** were only formed when old samples of anhydrous $FeCl_3$, that may contain traces of water, were used. It has been reported that the oxidative coupling reactions of phenols could be carried out with $FeCl_3\cdot6H_2O$ in organic solution or $FeCl_3$ in aqueous solution.[13] When we used $FeCl_3\cdot6H_2O$ instead of anhydrous $FeCl_3$, we successfully obtained the C–C dimer **3** as the main product (47% yield) and only observed a trace amount of the 12-chlorinated compound **2** by TLC control.

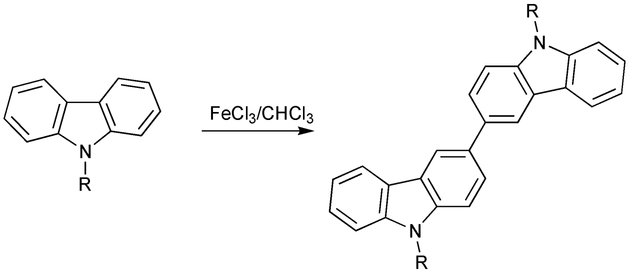

Fig. 1 Dimerization of carbazoles with $FeCl_3$.

Molecular oxygen does not react with ICZ **1**, but when the protons of **1** are abstracted with sodium hydride, the resulting dianion becomes very susceptible to oxygen in air, giving a dimer

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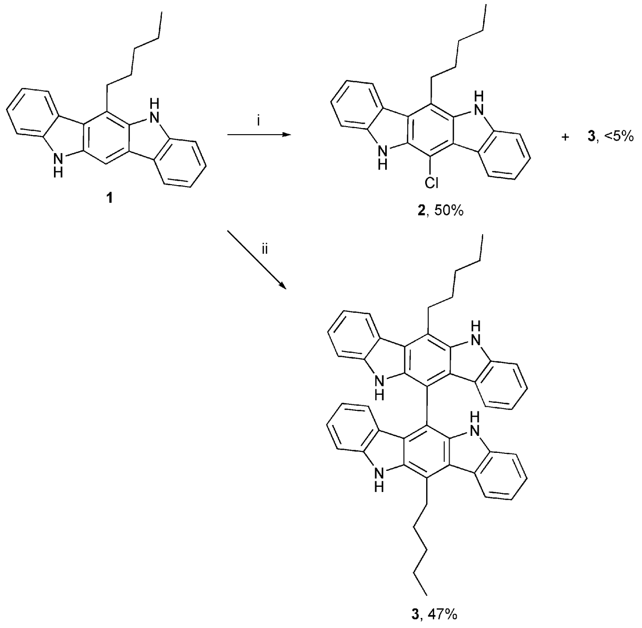
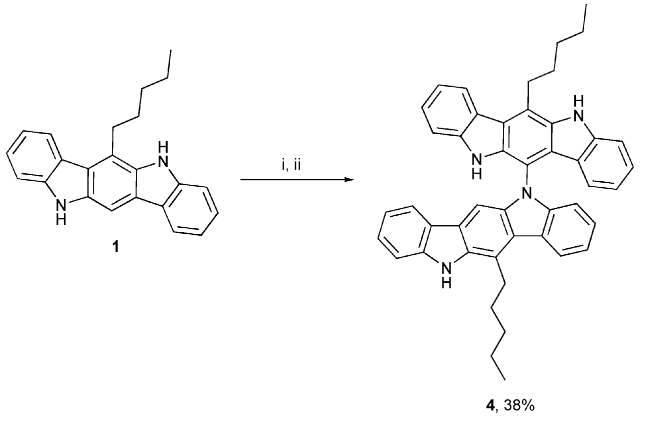


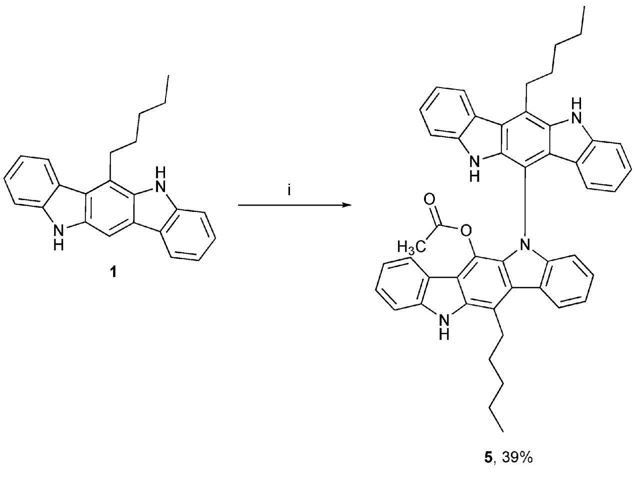
Scheme 1 (i) 6 Equiv. FeCl$_3$ anhydrous, dry chloroform, N$_2$ protection, rt, overnight. (ii) 1.5 Equiv. FeCl$_3$·6H$_2$O, chloroform, N$_2$ protection, rt, overnight.

with the same molecular mass as compound **3** (m/z 651 [M + H]$^+$), but clearly different in structure as evidenced by its NMR spectrum, showing lower symmetry. In fact, we observed that this dimer formed in some cases as a side reaction on attempted N-tosylation of **1**.[9] Under optimised conditions, involving formation of the dianion under an inert atmosphere at lower temperature and the subsequent passing of air at 70 °C, we obtained the C–N coupled dimer **4** (Scheme 2) in 38% yield. When oxygen is present from the beginning of the reaction, the yield of **4** is substantially lower.



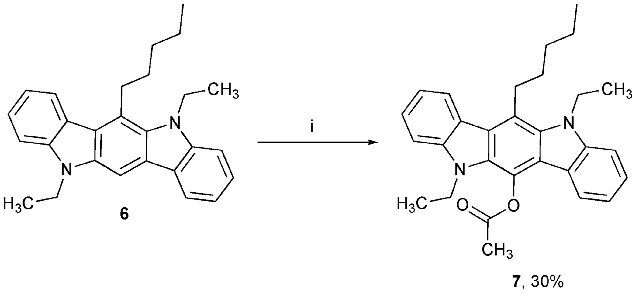
Scheme 2 (i) 4 Equiv. NaH, THF, N$_2$ protection, 0 °C then 70 °C. (ii) Air, 70 °C.

It is known that aromatic compounds may be oxidatively coupled to biaryls, polyaryls, or ring-closed compounds with stoichiometric amounts of palladium(II).[14] When the compound **1** was heated at reflux with 1.5 equivalents of Pd(OAc)$_2$ in acetic acid (Scheme 3), we obtained the compound **5** in 39% yield. Although basically this was also a C–N coupled dimer, both the MS and NMR spectra pointed to the uptake of an acetoxy group at the 12-position of the lower ICZ moiety. Since both the C–N dimer bond and the acetoxy group have hindered rotation, two conformers (1 : 1 ratio) can be observed in the ^{1}H-NMR spectra. On heating at 105 °C, rotation is fast and only one signal per hydrogen is observed (Fig. 2).



Scheme 3 (i) 1.5 Equiv. Pd(OAc)$_2$, AcOH, N$_2$, reflux overnight.

Thus, ICZ **1** showed very different behaviour towards oxidizing reagents as compared to the carbazole analogues. This may be due to the fact that the nitrogens of **1** are unsubstituted. Alkylated derivatives of **1**, available from our earlier work, could have a different reactivity. Therefore, we attempted to oxidize the N,N'-diethyl ICZ derivative **6** in the presence of FeCl$_3$ (hexahydrate or anhydrous) but no reaction was observed. On the other hand, when the compound **6** was treated with Pd(OAc)$_2$ as described in Scheme 3, we obtained the 12-O-acetyl derivative **7** in 30% yield (Scheme 4).



Scheme 4 (i) 1.5 Equiv. Pd(OAc)$_2$, AcOH, N$_2$, reflux overnight.

X-Ray crystal structures of 4 and 5

The structures of compounds **4** and **5** (Fig. 3) were determined by single crystal X-ray diffraction. Compounds **4** and **5** were crystallized from acetone (by slow evaporation) and chloroform (by vapor diffusion), respectively. X-Ray crystallographic analysis showed that compound **4** had a triclinic and **5** a monoclinic crystal system. For compound **4**, the asymmetric unit contains one dimer and three acetone molecules, which are hydrogen bonded with their O-atom to the three ICZ free N-atoms. However, for compound **5**, the asymmetric unit contains one dimer and one chloroform molecule and the oxygen atom of the O-acetyl group is hydrogen

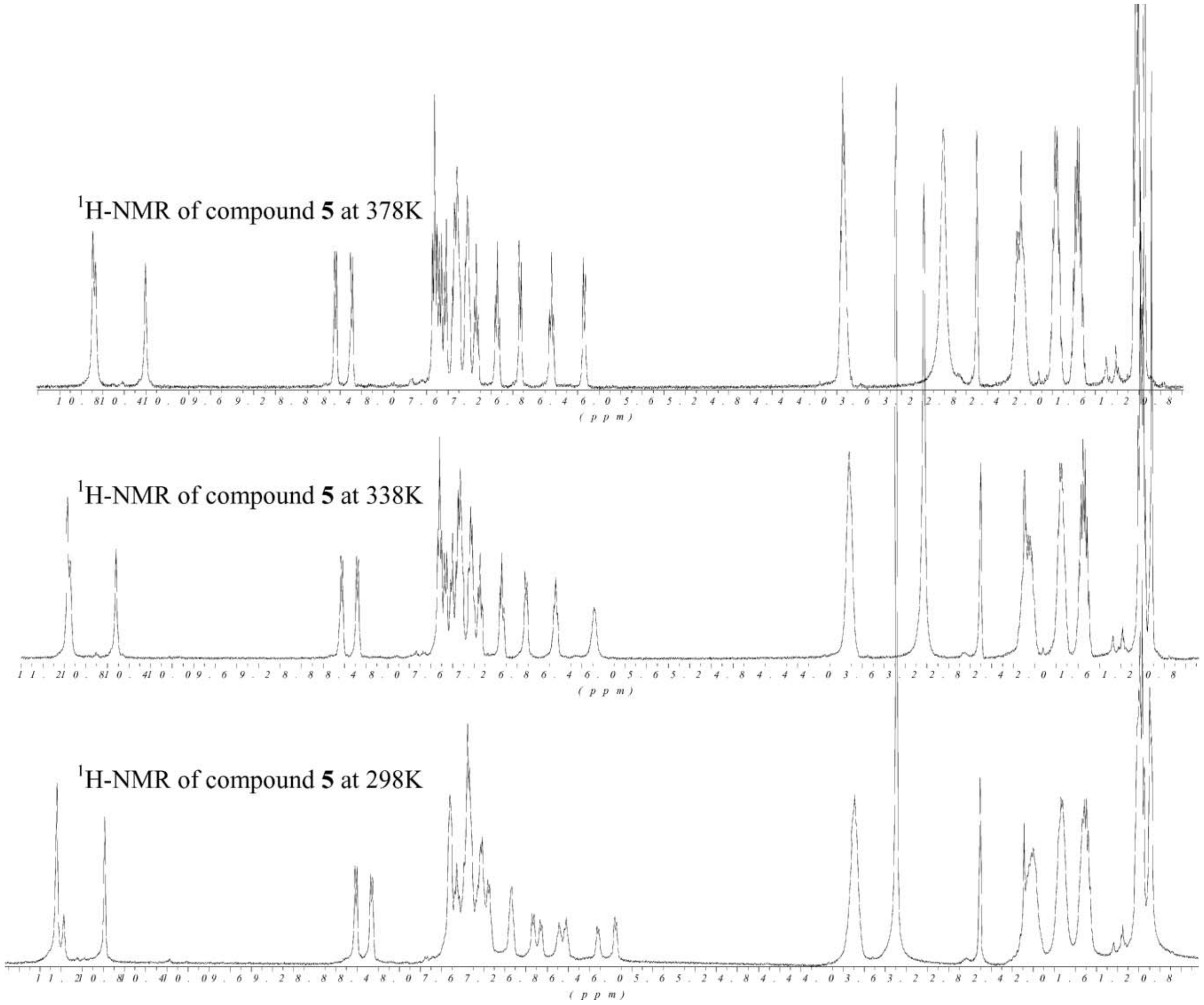


Fig. 2 ^{1}H-NMR spectra of compound **5** at 298 K, 338 K and 378 K.

bonded to a free nitrogen of the same ICZ moiety of another dimer molecule, linking the dimers together in the packing along the *b*-axis. The 6-pentyl indolo[3,2-*b*]carbazole moieties in the dimer are torsioned, with respect to each other and the angle between the planes through all five aromatic rings is 69.9° and 79.2° for compounds **4** and **5**, respectively.

Conclusions

In conclusion, we have developed methods to prepare new dimers of 6-monosubstituted 5,11-dihydroindolo[3,2-*b*]carbazole by oxidative coupling reactions. $FeCl_3 \cdot 6H_2O$ was an efficient reagent to synthesize 12,12′ C–C coupled dimers of 6-monosubstituted ICZ and anhydrous $FeCl_3$ can be used to regioselectively prepare 12-chlorinated ICZs. The C–N dimers of ICZ were obtained for the first time using oxidative coupling reactions with air or $Pd(OAc)_2$. No dimerizations were observed when *N*,*N*′-disubstituted ICZ was treated with the methods described above.

Experimental

General

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 300 (300 MHz) or a Bruker AMX-400 (400 MHz) spectrometer. 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 Micromass Mattro II instrument (ES). High-resolution mass spectra were recorded on a KRATOS MS50TC instrument. 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–Kα radiation (λ = 1.54178 Å). Commercially available reagents were used as received.

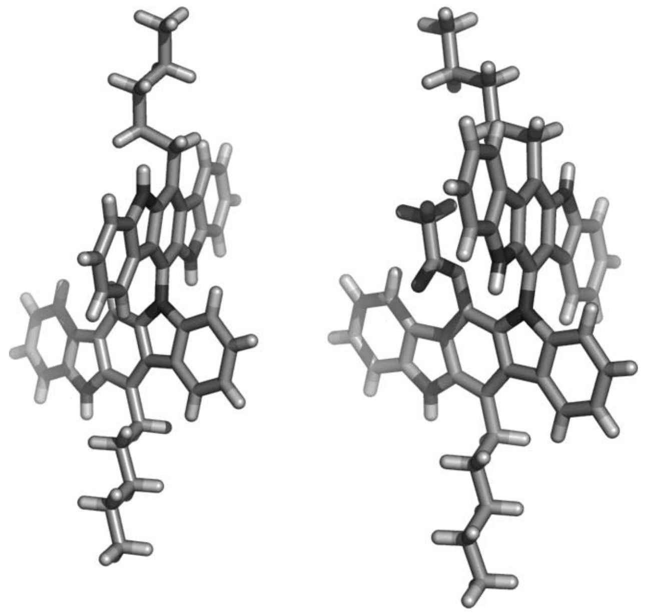


Fig. 3 (a) X-Ray structure of compound **4**. (b) X-Ray structure of compound **5**.

6-Chloro-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (2). To a solution of compound **1** (0.2 g, 0.6 mmol) in dry chloroform (5 ml) was added $FeCl_3$ (0.6 g, 3.7 mmol). The reaction mixture was stirred at room temperature overnight under nitrogen. After addition of H_2O (10 ml), the aqueous solution was extracted with EtOAc (3 × 20 ml). The combined organic solvents were removed and the crude compound was purified with silica gel chromatography (EtOAc–heptane, 2 : 8) to give compound **2** (0.11 g, 50%) as a light yellow solid, mp 212–214 °C. δ_H (300 MHz, DMSO, Me_4Si): 0.88 (t, 3H, CH_3), 0.13–1.14 (m, 2H, CH_2), 1.55 (br, 2H, CH_2), 1.81 (br, 2H, CH_2), 3.49 (br, 2H, CH_2), 7.21 (m, 2H, *J* 6.8, 6.9, 2 × CH), 7.44 (m, 2H, *J* 7.2, 7.4, 2 × CH), 7.57 (m, 2H, 2 × CH), 8.14 (d, 1H, *J* 7.78, CH), 8.52 (d, 1H, *J* 7.80, CH), 11.25 (s, 1H, NH), 11.28 (s, 1H, NH); δ_C (75 MHz, DMSO, Me_4Si): 14.9, 23.2, 28.9, 29.6, 32.4, 107.4, 111.6, 112.1, 118.3, 118.9, 119.0, 121.9, 122.4, 122.8, 122.9, 123.5, 125.2, 126.4, 126.8, 133.4, 135.4, 142.0, 144.3; MS (CI): *m/z* 361 ($[M + H]^+$, 100%), 363 ($[M + H]^+$, 32).

12,12′-Bis(6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole) (3). To a solution of compound **1** (0.2 g, 0.6 mmol) in chloroform (5 ml) was added $FeCl_3{\cdot}6H_2O$ (0.25 g, 0.9 mmol). The reaction mixture was stirred at room temperature overnight under nitrogen. After addition of H_2O (10 ml), the aqueous solution was extracted with EtOAc (3 × 20 ml). The combined organic solvents were removed and the crude compound was purified with silica gel chromatography (EtOAc–heptane, 2 : 8) to give compound **3** (0.095 g, 47%) as a brown solid, mp 272–274 °C. δ_H (400 MHz, DMSO, Me_4Si): 0.99 (t, 6H, 2 × CH_3), 1.48–1.55 (m, 4H, 2 × CH_2), 1.71–1.75 (m, 4H, 2 × CH_2), 1.99–2.09 (m, 4H, 2 × CH_2), 3.69–3.73 (m, 4H, 2 × CH_2), 6.21 (d, 2H, *J* 7.78, 2 × CH), 6.74 (t, 2H, *J* 7.45, 2 × CH), 7.09 (t, 2H, *J* 7.51, 2 × CH), 7.16–7.18 (m, 2H, 2 × CH), 7.27–7.28 (m, 4H, 4 × CH), 7.42 (d, 2H, *J* 8.00, 2 × CH), 8.25 (d, 2H, *J* 7.81, 2 × CH), 10.23 (s, 2H, NH), 11.10 (s, 2H, NH); δ_C (75 MHz, DMSO, Me_4Si): 14.5, 22.8, 28.9, 29.3, 32.1, 109.5, 110.5, 111.1, 117.4, 118.0, 118.2, 120.6, 120.9, 121.1, 122.1, 123.2, 123.4, 124.9, 125.0, 134.9, 135.0, 141.6, 141.9; HRMS (EI): *m/z* calcd for $C_{46}H_{42}N_4$ $[M]^+$: 650.34095; found: 650.34037.

5-(12′-Pentyl-5′,11′-dihydroindolo[3,2-*b*]carbazole-6′-yl)-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (4). To a solution of compound **1** (0.3 g, 0.9 mmol) in THF (5 ml) was added NaH (0.15 g, 3.7 mmol) in portions while protecting with nitrogen at 0 °C. The reaction mixture was warmed to room temperature slowly and then heated at 70 °C for 3 h under nitrogen. After removing the nitrogen protection, air was bubbled through the reaction vessel and the reaction mixture was heated for 1 h at 70 °C. After work-up with addition of NH_4Cl aq. (15 ml), the aqueous solution was extracted with EtOAc (3 × 15 ml). The combined EtOAc solutions were evaporated and the residue was purified with silica gel chromatography (CH_2Cl_2–heptane, 1 : 1) to give compound **4** (0.115 g, 38%) as a light yellow solid, mp 171–173 °C. δ_H (400 MHz, DMSO, Me_4Si): 0.98–1.02 (m, 6H, 2 × CH_3), 1.50–1.57 (m, 4H, 2 × CH_2), 1.71–1.79 (m, 4H, 2 × CH_2), 2.05 (br, 4H, 2 × CH_2), 3.70–3.74 (m, 4H, 2 × CH_2), 6.05 (d, 1H, *J* 7.90, CH), 6.46 (t, 1H, *J* 7.52, CH), 6.80 (d, 1H, *J* 7.96, CH), 6.89 (r, 1H, *J* 7.44, CH), 7.14 (t, 1H, *J* 7.16, CH), 7.16–7.39 (m, 7H, 7 × CH), 7.48–7.51 (m, 2H, 2 × CH), 7.81 (d, 1H, *J* 7.81, CH), 8.28 (d, 1H, *J* 7.99, CH), 8.43 (d, 1H, *J* 7.77, CH), 10.79 (s, 1H, NH), 11.06 (s, 1H, NH), 11.30 (s, 1H, NH); δ_C (75 MHz, DMSO, Me_4Si): 14.1, 22.4, 28.6, 29.0, 31.8, 97.0, 109.3, 110.5, 111.0, 117.6, 118.3, 119.0, 119.1, 119.5, 119.8, 120.3, 120.4, 120.64, 121.2, 121.6, 121.9, 122.2, 122.4, 122.6, 122.9, 123.2, 125.1, 125.2, 125.4, 1338, 134.7, 134.8, 136.5, 141.3, 141.2, 141.5, 141.8; HRMS (EI): *m/z* calcd for $C_{46}H_{42}N_4$ $[M]^+$: 650.34095; found: 650.34051.

5-(12′-Pentyl-5′,11′-dihydroindolo[3,2-*b*]carbazole-6′-yl)-6-acetoxy-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (5). A mixture of compound **1** (0.15 g, 0.46 mmol) and $Pd(OAc)_2$ (0.15 g, 0.67 mmol) in acetic acid (5 ml) was heated at reflux overnight. After removal of the acetic acid *in vacuo*, the residue was dissolved in EtOAc (30 ml) and washed with $NaHCO_3$ (2 × 15 ml). The organic solvent was evaporated and the crude compound was purified with silica gel chromatography (EtOAc–heptane, 2 : 8) to give the compound **5** (0.064 g, 39%) as a brown solid, mp 174–175 °C. δ_H (400 MHz, DMSO, Me_4Si): 0.9 (s, 3H, CH_3), 0.95–1.02 (m, 6H, 2 × CH_3), 1.48–1.54 (m, 4H, 2 × CH_2), 1.72–1.74 (m, 4H, 2 × CH_2), 1.99–2.03 (m, 4H, 2 × CH_2), 3.68–3.70 (m, 4H, 2 × CH_2), 5.95–6.12 (d, 1H, *J* 7.58, CH), 6.41–6.51 (m, 1H, CH), 6.66–6.75 (d, 1H, *J* 7.62, CH), 7.69 (br, 1H, CH), 7.15–7.53 (m, 10H, 10 × CH), 8.27 (d, 1H, *J* 7.71, CH), 8.41 (d, 1H, *J* 7.80, CH), 10.80 (s, 1H, NH), 11.19–11.25 (d, 1H, NH), 11.25 (s, 1H, NH); δ_C (75 MHz, DMSO, Me_4Si): 14.1, 14.2, 18.3, 22.4, 22.5, 28.4, 29.0, 31.7, 99.8, 109.6, 110.3, 110.6, 110.9, 111.0, 111.2, 115.2, 115.5, 116.5, 116.6, 117.4, 117.6, 118.1, 118.3, 119.1, 119.2, 119.7, 120.1, 120.5, 120.6, 120.7, 120.8, 121.0, 121.1, 121.2, 121.5, 121.8, 121.9, 122.2, 122.4, 122.6, 122.7, 123.1, 125.1, 125.3, 125.6, 125.8, 126.9, 127.0, 133.6, 134.2, 134.4, 135.0, 141.0, 141.2, 141.4, 141.6, 142.2, 142.3, 167.4, 167.8; HRMS (EI): *m/z* calcd for $C_{48}H_{44}N_4O_2$ $[M]^+$: 708.34643; found: 708.34747.

6-Acetoxy-5,11-diethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (7). A mixture of compound **6** (0.05 g, 0.13 mmol) and $Pd(OAc)_2$ (0.05 g, 0.22 mmol) in acetic acid (4 ml) was heated at reflux overnight. After removal of the acetic acid *in vacuo*, the residue was dissolved in EtOAc (30 ml) and washed with NaHCO$_3$ (2 × 15 ml). The organic solvent was evaporated and the crude compound was purified with silica gel chromatography (EtOAc–heptane, 2 : 8) to give the compound **7** (0.017 g, 30%) as a brown solid. δ_H (300 MHz, DMSO, Me$_4$Si): 0.96 (t, 3H, CH$_3$), 1.34 (m, 3H, CH$_3$), 1.43 (m, 8H, 2 × CH$_3$, CH$_2$), 1.66 (br, 2H, CH$_2$), 1.86 (br, 2H, CH$_2$), 3.60 (br, 2H, CH$_2$), 4.60 (m, 4H, 2 × CH$_2$), 7.19–7.27 (m, 2H, 2 × CH), 7.50 (m, 2H, 2 × CH), 7.76–7.65 (m, 2H, 2 × CH), 7.96 (d, 1H, *J* 7.7, CH), 8.18 (d, 1H, *J* 7.8, CH); MS (CI): m/z 441 $[M + H]^+$.

X-Ray structure determination of 4 and 5

For the structures of compounds **4** and **5**, intensity data were collected on a SMART 6000 diffractometer equipped with CCD detector using Cu–Kα radiation (λ = 1.54178 Å). The images were interpreted and integrated with the program SAINT from Bruker.[15] Both structures were solved by direct methods and refined by full-matrix least-squares on $F2$ using the SHELXTL program package.[16] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U (eq) of the parent atoms (1.5 times for methyl groups).†

Single crystal strucutre of 4. $C_{55}H_{60}N_4O_3$, crystal size 0.5 × 0.3 × 0.2 mm^3, M = 825.07, triclinic, $P\bar{1}$, a = 12.4498(7), b = 13.0721(6), c = 17.1213(8) Å, α = 76.028(3), β = 88.352(4), γ = 64.368(3), V = 2428.7(2) Å^3, T = 100(2) K, Z = 2, D_c = 1.128 g cm^{-3}, μ(Cu–Kα) = 0.542 mm^{-1}, F(000) = 884, 8852 independent reflections (R_{int} = 0.0312); final R = 0.0711 for 7354 reflections with $I > 2\sigma(I)$ and $\omega R2 = 0.1497$ (all data); a disordered acetone molecule in a void of 261 Å^3 at position (0.5, 0.553, 0.5), was modelled with SQUEEZE[15] (total contribution of 44 e$^-$).

Single crystal structure of 5. $C_{49}H_{45}Cl_3N_4O_2$, crystal size 0.3 × 0.25 × 0.25 mm^3, M = 828.24, monoclinic, $C2/c$, a = 24.3549(8), b = 13.9993(4), c = 26.1244(7) Å, β = 94.689(2), V = 8877.3(5) Å^3, T = 100(2) K, Z = 8, D_c = 1.239 g cm^{-3}, μ(Cu–Kα) = 2.204 mm^{-1}, F(000) = 3472, 7781 independent reflections (R_{int} = 0.1040); final R = 0.0776 for 5097 reflections with $I > 2\sigma(I)$ and $\omega R2 = 0.1793$ (all data); a completely disordered solvent molecule (CHCl$_3$) in a void of 143 Å^3 at position (0, 0, 0), was modelled with SQUEEZE[17] (total contribution of 55 e$^-$).

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