Direct Synthesis of 2,8- and 3,9- *Bis*bromine-functionalised Indolo[3,2-b]carbazoles

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Two indolo[3,2-b]carbazoles disubstituted in 2,8- or 3, 9- positions with bromine atoms were prepared in good yields by condensation of 5-bromoindole or 6-bromoindole with benzaldehyde using hydroiodic acid as catalyst followed by aromatization with iodine. The structures of compounds were proved by FT-IR, ^{1}H-, ^{13}C-, and mass spectroscopy.

Keywords: indolocarbazoles, synthesis, bisbromine functionalised, spectral characterization

Among the five members of indolocarbazole family, indolo[3,2-b]carbazole (ICZ) isomer has attracted considerable interest in the last years for organic electronics [1, 2]. It is analogue of carbazole and contains indole unit fused to the 2,3 positions of one of the benzenoid rings of the carbazole moiety and the two nitrogen atoms are in *ex situ* each to other yielding to a rigid and coplanar structure with a more extended conjugation, stronger electron donating character and higher charge carrier mobility compared to carbazole [3-5]. Functionalized ICZs are used as building blocks for synthesis of new hole-transport materials having good thermal and photochemical stability and applications in electrophotography [6], organic field effect transistors [7-13], organic light emitting diodes [13-17], photovoltaic solar cells [11, 18, 19], and dye-sensitized solar cells [20].

The building of ICZ framework was performed by a number of synthetic methods and the advance in literature until 2008 has been overviewed in some reviews [21, 22]. The most old and common method used to synthesize indolo[3,2-b]carbazole skeleton is based on double Fischer indolisation of cyclohexane-1,4-dione *bis* phenylhydrazone by treatment with a mixture of glacial acetic and concentrated sulphuric acid [23]. However, the linear isomer is obtained in low to moderate yields and is accompanied by side products (angular isomer). Acid-catalyzed condensation of indole with aliphatic aldehydes is an alternative route used by Bergman and Tholander to build 6,12-disubstituted ICZ moiety [24]. Furthermore, Dehaen et al [25, 26] have reported a three-stage one-pot approach toward 6-monosubstituted- or 6,12-disubstituted-5,11-dihydroindolo[3,2-b]carbazoles in moderate to good yields (20-50%). The synthesis is based on the condensation of an indole and an aldehyde using iodine as catalyst, followed by intramolecular cyclization with an *ortho* ester in presence of strong acids. In 2008 Deb and Bhuyan have reported the synthesis of [3,2-b] ICZs from 3,3'-bis(indolyl)methane in the presence of iodine as catalyst in refluxing acetonitrile [27]. The 3,3'-*bis*(indolyl)methane was obtained from two moles of indole and one mole of aldehyde in presence of iodine at room temperature and very short time [27]. In 2009, Dehaen et al have reported a facile and general two-step method towards 6,12-diaryl-5,11-dyhydroindolo[3,2-b]carbazoles by condensation of indole and aromatic aldehyde using hydroiodic acid as catalyst and aromatization of intermediary product with iodine [28].

Although for synthesis of indolo[3,2-b]carbazole ([3,2-b]ICZ) skeleton were developed some efficient methods, a literature overwiew reveals only a few reports on the synthesis of *bis*bromine-functionalized ICZs. Yudina and Bergman [29] have synthesized 2,8-dibromo ICZ under conditions described by Robinson [23] but starting from 4-bromophenylhydrazine and 1,4-cyclohexanedione while 3,9-dibromo ICZ was synthesized by the same route using 3-bromophenylhydrazine and 1,4-cyclohexanedione [7, 8]. Leclerc et al have reported synthesis of 2,8- and 3,9-chlorine disubstituted ICZ by Cadogan ring-closure reaction with very low overall yields (6 and 7 %) [30]. Synthesis of bromine-functionalized ICZ by direct bromination of ICZ with N-bromosuccinimide (NBS) or bromine was tried but results are contradictory. First, Dehaen and Snick have reported that direct bromination of 5,11-dihexyl 6,12-diphenyl [3,2-b]ICZ with NBS in acetic acid was inefficient, the initial product being recovered [31]. However, they claimed that the bromination of 2,8-dibromo 5,11-dihexyl-6,12-diphenyldihydro[3,2-b] ICZ (the intermediary compound in synthesis of ICZ) in the same experimental conditions yielded to expected 2,8-dibromo ICZ derivative [31]. On the other hand, Cai et al. have reported the synthesis of 2-bromo-5,11-dihexyl-6,12-diphenyl[3,2-b]ICZ by direct bromination of ICZ with NBS in CCl_4 [20]. Anyhow, if the direct bromination is possible only ICZs functionalized at 2, 8 positions should be obtained because the lone pair electrons of nitrogen atoms activate the *para* positions for electrophylic aromatic substitution.

In this work we report the successful synthesis and characterization of two compounds: 2,8-dibromo-5,11-di(2-ethylhexyl)-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**1c**) and 3,9-dibromo-5,11-bis(2-ethylhexyl)-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**2c**) (scheme 1) using bromine-substituted indoles as starting compounds. These compounds will be used as monomers in synthesis of indolocarbazole polymers by various polycondensation reactions to obtain electroactive polymers.

Experimental part

Materials and instruments

All starting organic compounds, 5-bromoindole (99%), 6-bromoindole (96%), benzaldehyde, tetraethyl

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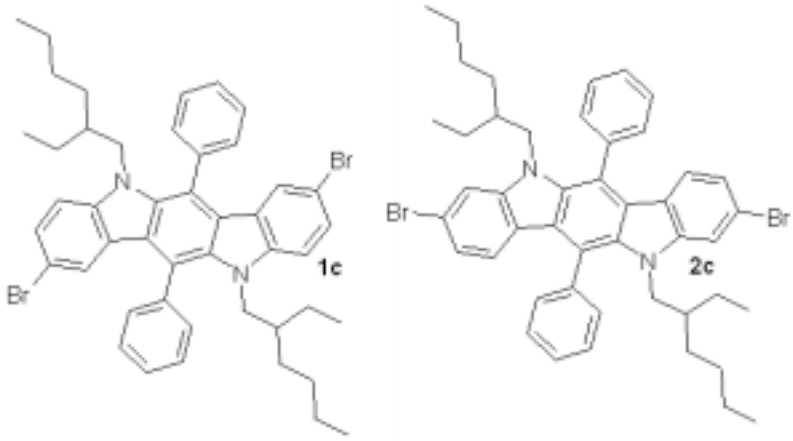


Scheme 1. Chemical structures of 2,8-dibromo-5,11-di(2-ethylhexyl)-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole. (**1c**) and 3,9-dibromo-5,11-bis(2-ethylhexyl)-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**2c**)

ammonium bromide, HI (57%), 2-ethylhexyl bromide, and iodine and solvents were purchased from Sigma-Aldrich and used without further purification.

^{1}H and ^{13}C- NMR spectra were recorded at room temperature with a Bruker Avance DRX-400 spectrometer (400 MHz or 100 MHz) as solutions in $CDCl_3$ or dimethyl sulfoxide (DMSO) and tetramethylsilane as an internal standard. UV-visible and fluorescence measurements were carried out in $CHCl_3$ solutions with a Specord 200 spectrophotometer and Perkin Elmer LS 55 apparatus, respectively. ESI-MS analysis was performed using an AG-QTOF instrument and methanol/chloroform as solvent.

*2,8-dibromo-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**1b**)*

Equimolar amounts of 5-bromoindole (2.5 g, 12.75 mmol) and benzaldehyde (1.35 g, 12.75 mmol) were charged to a 100 mL round-bottom flask and dissolved in acetonitrile (10 mL). While stirring, HI (57%) (0.126 g, 1.27 mmol) was added dropwise and the reaction mixture was maintained at room temperature for 18 h then allowed to heat at 80°C for 7 h. After that the formed precipitated was filtered off and washed with cold acetonitrile and dried to yield 2.77 g product. It is a mixture of 2,8-dibromo-6,12-diphenyl-5,6,11,12-tetrahydroindolo[3,2-b]carbazole (only isomer *trans*) (**1a**) and 2,8-dibromo-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**1**). For complete aromatization, the product was suspended in acetonitrile (50 mL) and iodine (0.50 g, 2 mmol) was added. The reaction mixture was heated at 80°C for 28 h. The precipitate was filtered off, washed with cold acetonitrile and dried until constant weight, to give 1.8 g compound **1** (50% yield) as yellow solid. M.p.>250 °C. ESI-MS: m/z= 566.9844

^{1}H-NMR (400 MHz, DMSO-d_6), δ: 7.10 (s, 2H), 7.41 (s, 2H), 7.69-7.78 (m, 10H), 10.66 (s, 2H, -NH),

^{13}C-NMR (400 MHz, DMSO-d_6), δ: 108.96, 112.58, 117.00, 119.37, 123.18, 123.69, 127.26, 127.84, 128.89, 129.46, 133.76, 135.97, 140.28

FTIR (KBr, cm^{-1}): 3429, 3065, 3027, 1603, 1540, 1449, 1349, 1277, 1213, 1140, 1089, 1059, 1027, 878, 805, 781, 704, 672, 567 cm^{-1}.

UV-vis (THF) λ_{ab}^{max}: 287, 329, 344, 403, 424 nm; λ_{em}^{max}: 451 nm

*3,9-dibromo-6,12,diphenyl 5,11-dihydroindolo[3,2-b]carbazole (**2b**)*

3,9-dibromo-6,12, 5,11-dihydroindolo[3,2-b]carbazole was synthesized from 6-bromoindole and benzaldehyde by the same procedure as described for 2,8-dibromo-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole. The yield is 42 %. M.p. >250 °C. ESI-MS: m/z=566.9821

^{1}H-NMR (400 MHz, DMSO-d_6), δ: 6.94-7.01 (d, 4H), 7.60 (s, 2H), 7.65-7.79 (m, 10H), 10.74 (s, 2H, -NH)

^{13}C-NMR (400 MHz, DMSO-d_6), δ: 113.59, 117.20, 118.17, 119.71, 120.32, 121.22, 122.62, 128.32, 129.44, 129.87, 133.80, 136.32, 142.66

FTIR (KBr, cm^{-1}): 3424, 3056, 3022, 1604, 1536, 1435, 1349, 1305, 1211, 1147, 1053, 1026, 919, 840, 803, 775, 749, 704, 584, 519 cm^{-1}.

UV-vis (THF) λ_{ab}^{max}: 286, 330, 347, 394, 415 nm; λ_{em}^{max}: 442 nm

*2,8-dibromo-5,11-di(2-ethylhexyl)-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**1c**)*

In a two-necked round bottom flask equipped with a dropping funnel and magnetic stirring bar were introduced **1b** (1.2 g, 2.13 mmol), tetraethyl ammonium bromide ($(C_2H_5)_4NBr$, 3.5 mg, 0.01 mmol) and DMSO (50 mL). A solution of NaOH (3.5 mL, 50% w/w) was added dropwise under Ar atmosphere and stirred for 30 min, followed by addition of 2-ethylhexyl bromide (1.64 g, 8.54 mmol). The reaction mixture was stirred at ambient temperature overnight and then heated to 55°C and maintained at this temperature for 4 h. Subsequently the reaction mixture was cooled down to room temperature and poured into 400 mL methanol with stirring, neutralized with a solution of HCl (1M). The precipitated yellow-green solid was filtered and washed with methanol 3 times, and dried until constant weight. The yellow-green solid was obtained with a yield of 1.9 g, 70%. ESI-MS: m/z= 791.2312

^{1}H-NMR (400 MHz, $CDCl_3$), δ: 0.58-0.95 (m, 10H), 1.04-1.32 (m, 8H), 1.71 (m, 4H), 3.81 (d, 2H), 6.4 (d, 2H), 7.1 (d, 2H), 7.3 (dd, 2H), 7.62-7.73 (m, 10H).

^{13}C-NMR (400 MHz, $CDCl_3$), δ: 10.42, 14.00, 23.04, 23.14, 28.16, 29.84, 39.16, 48.44, 110.49, 110.52, 118.45, 122.59, 124.34, 125.14, 127.76, 128.54, 129.11, 129.14, 131.12, 133.24, 138.02, 141.98

FTIR (KBr, cm^{-1}): 3057, 3026, 2956, 2926, 2862, 1599, 1518, 1458, 1443, 1340, 1283, 1228, 1165, 1098, 1067, 1024, 876, 791, 732, 702, 645, 586 cm^{-1}.

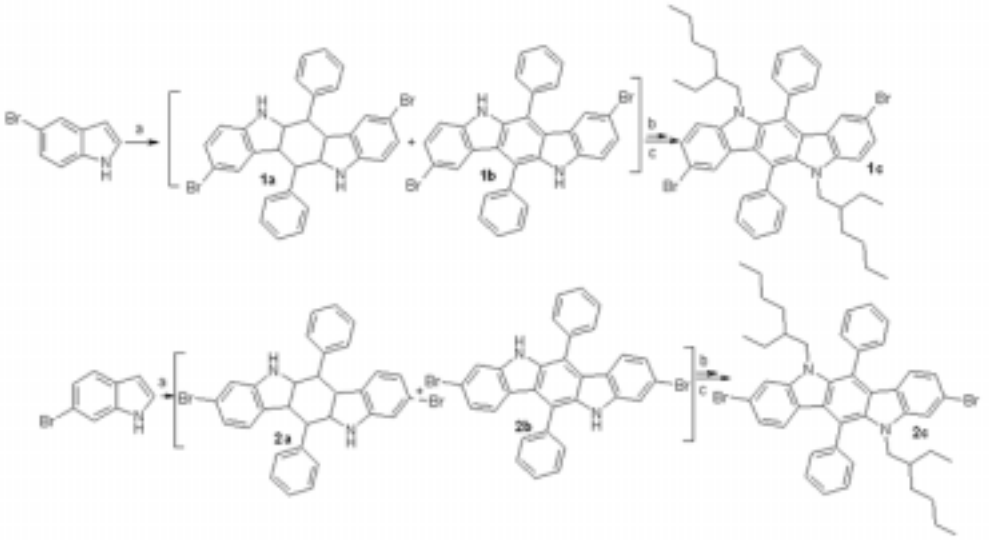
UV-vis (THF) λ_{ab}^{max}: 294, 329, 344, 406, 431 nm; λ_{em}^{max}: 441 nm and a shoulder at 467 nm

*3,9-dibromo-5,11-bis(2-ethylhexyl)-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**2c**)*

The compound was synthesized according to the general procedure for the ***1c*** and was obtained as yellow solid (72 % yield). ESI-MS: m/z= 791.2231

^{1}H-NMR (400 MHz, $CDCl_3$), δ: 0.58-0.95 (m, 10H), 1.05-1.07 (m, 8H), 1.43 (s, 2H) 1.85 (m, 4H), 3.74 (d, 2H), 6.19-6.21 (d, 2H), 6.87-6.89 (d, 2H), 7.39 (s, 2H), 7.62-7.68 (m, 10H).

^{13}C-NMR (400 MHz, $CDCl_3$), δ: 10.45, 13.96, 23.02, 23.09, 25.61, 27.97, 29.65, 30.32, 39.05, 48.39, 67.97, 112.08,



Scheme 2. Synthesis of indolo[3,2-b]carbazole monomers. (a) benzaldehyde, CH_3CN, HI (57%), r.t. 18h and then 80°C for 7h. (b) CH_3CN, I_2, reflux, 3 days (c) DMSO, NaOH, 2-ethylhexyl bromide

129.01, 129.06, 131.18, 133.20, 138.19, 144.16

FTIR (KBr, cm^{-1}): 3075, 3055, 3024, 2959, 2928, 2873, 2857, 1597, 1521, 1460, 1435, 1382, 1352, 1314, 1230, 1163, 1066, 1024, 927, 888, 828, 797, 737, 703, 590 cm^{-1}.

UV-vis (THF) λ_{ab}^{max}: 297, 332, 348, 398, 421 nm; λ_{em}^{max}: 434 nm and a shoulder at 455 nm

Results and discussions

The structure of ICZ moiety allows tuning its properties by introduction of functional groups in many possible positions. The [3,2-b] ICZ isomer is currently disubstituted at carbons 2,8- and 3,9-, which are analogues with carbazole's positions 3,6 and 2,7, respectively. When ICZ is synthesized from indole and aldehyde [18, 19], positions 6 and 12 of ICZ are substituted and the nature of substituents is imposed by the aldehyde used in the condensation. In many cases, to increase the solubility of the monomers and polymers in common organic solvents and to decreases the intermolecular interactions, the two N-H sites of ICZ were substituted with long and branched alkyl chains or aromatic substituents. The connection position of ICZs in the polymer chain determines the conjugation length and allows easy tuning electronic and optical properties. Polymers containing [3,2-b]ICZ units connected in the conjugated main chain by positions 2 and 8 have less effective conjugation than polymers with 3,9-disubstituted [3,2-b]ICZ, where conjugation is through a terphenyl unit.

For the introduction of bromine functional groups at 2,8- or 3,9- of ICZ we proposed an alternative synthetic scheme based on the use of pre-functionalised indole derivatives containing bromine at 5- or 6- position. Interestingly, the bromine-substituted indoles, accessible commercial products, were not used in synthesis of functionalised ICZs. Therefore, as shown in Scheme 2, 5-bromoindole and 6-bromoindole (available commercial products) were used in condensation with equimolar quantities of benzaldehyde and in presence of 2% mole hydroiodic acid (57%) as catalyst to obtain the corresponding dibromine-substituted [3,2-b] ICZs as a mixture of aromatic and dihydro- isomers. The dihyro- compounds are composed from a mixture of trans (predominant) and cis isomers.

^{1}H-NMR spectra of compounds **1b** and **2b** presented in Figure1 and 2 prove their proposed structure for ICZ skeleton and show four signals, assigned to NH protons, protons of phenyl substituents and protons from ICZ group. Bromine substituent influences the peaks position of neighboring protons and NH protons.

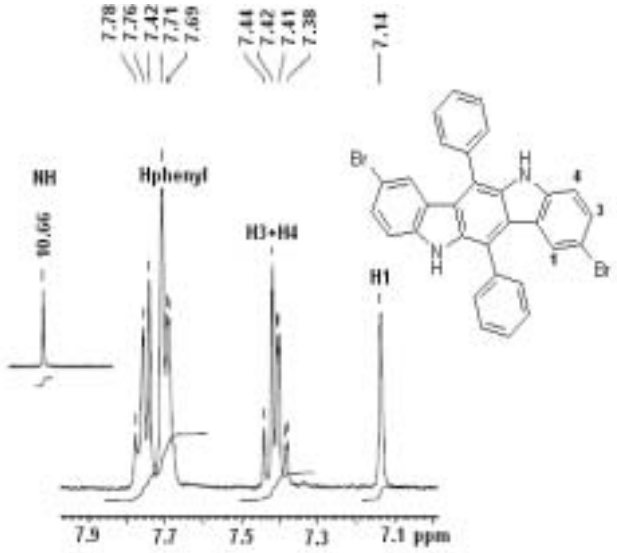


Fig. 1. ^{1}H-NMR spectrum (DMSO-d_6) of 2,8-dibromo-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**1b**)

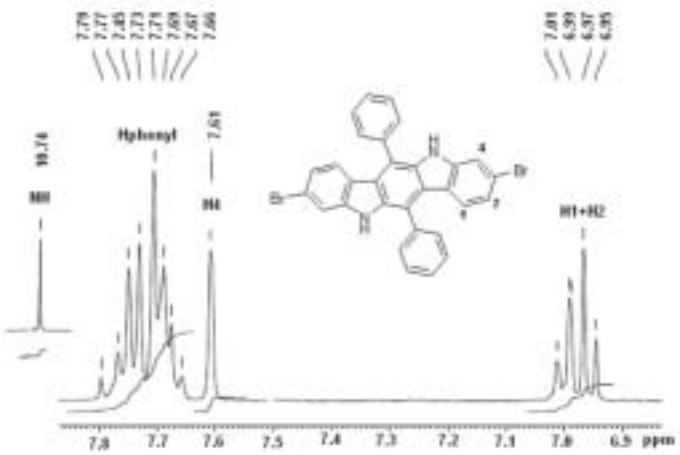


Fig. 2. ^{1}H-NMR spectrum (DMSO-d_6) of 3,9-dibromo-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**2b**)

Figure 3 and 4 shows the ^{13}C-NMR spectra of the two compounds with tentative assignments of signals, based on 2D-HMQC and COSY-NMR experiments.

Normalized UV absorption and fluorescence spectra of dilute solutions in THF of the synthesized compounds are shown in figure 5. All compounds show absorptions in the range of 240-470 nm, with two strong absorption peaks in the wavelength regions of 250-300 nm and 300-350 nm, respectively, which were assigned to the $\pi-\pi^*$ transition, while there were only weak absorptions beyond 400-440

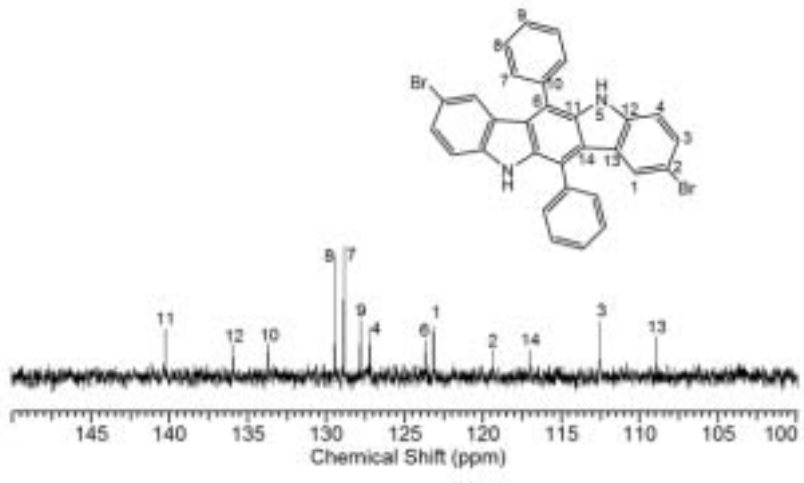


Fig. 3. ^{13}C-NMR spectrum (DMSO-d_6) of 2,8-dibromo-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**1b**)

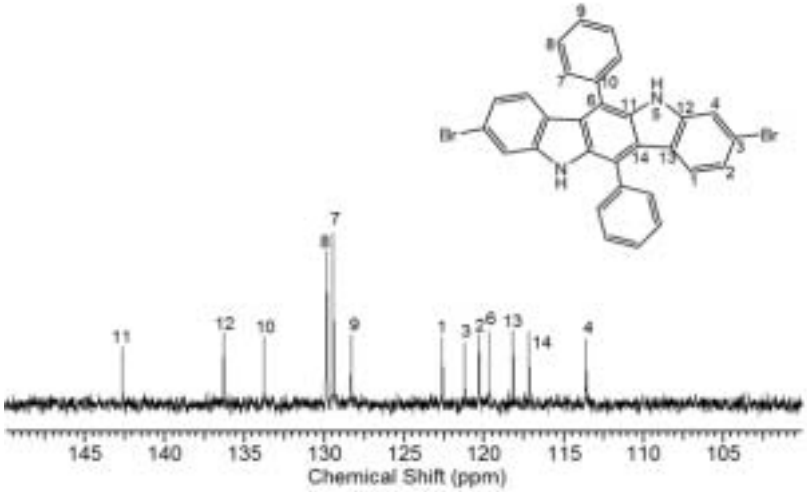


Fig. 4. ^{13}C-NMR spectrum (DMSO-d_6) of 3,9-dibromo-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**2b**)

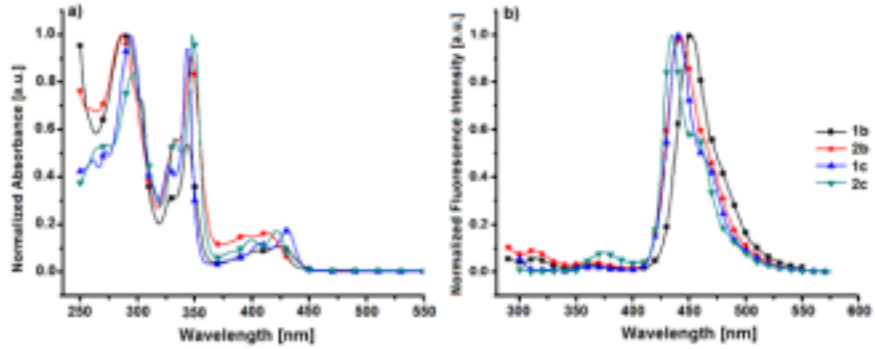


Fig. 5. UV-vis absorption (a) and fluorescence emission (b) spectra of dilute THF solutions (10^{-5} mol/L) of **1b**, **1c**, **2b** and **2c**

nm due to the n-π* transitions. The absorption spectra of **1b** (424 nm) and **1c** (431 nm) are red-shifted with respect of the corresponding **2b** (415 nm) and **2c** (421 nm) respectively, due to the effect of substitution on the electron delocalization of the molecules. In the same time, the introduction of alkyl groups at nitrogen atoms of ICZs has as result a slight bathocromic shifting (6-7 nm) of UV spectrum with that of the corresponding non-alkylated derivatives due to the electron donating of alkyl groups.

The fluorescence spectra of 2,8- and 3,9-dibromoICZs have similar shape with maxima at 451 nm for **1b** and 442 nm for **2b**, assigned to emission from indolcarbazole group (λ_{ex} = 286 nm). They are independent of the wavelength of excitation. The spectra of alkylated compounds (**1c** and **2c**) are slightly blue shifted with respect of the corresponding non-alkylated derivatives **1b** and **2b**, respectively, having emission maximum at 441 nm with a shoulder at 467 nm for compound **1c** and 434 nm with a shoulder at 455 nm for compound **2c**.

Conclusions

We report here a very simple and efficient procedure for the synthesis dibromoindolo[3,2-b]carbazoles or dibromoindolo[2,3-b]carbazoles from the reaction of bromindole derivatives with benzaldehyde using in a first stage hydroiodic acid (HI, 57%) as a catalyst, obtaining a mixture of 2,8- or 3,9-dibromo-6,12-diphenyl-5,6,11,12-tetrahydroindolo[3,2-b]carbazole (**1a**, **2a**) and 2,8- or 3,9-dibromo-6,12-diphenyl-6,12-dyhydroindolo[3,2-b]carbazole (**1b**, **2b**), then iodine was used as an oxidation reagent to convert **1a** and **2a** to **1b** and **2b**. Alkylation of NH group was carried out with 2-ethylhexyl bromide in DMSO using NaOH and alkylated compounds are soluble in chloroform.

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References

1. BOUDREAULT, P.L., BEAUPRE, S., LECLERC, M., Polym. Chem., **1**, 2010, p. 127.
2. WAKIM, S., AICH, B.R. TAO, Y., LECLERC, M., Polym. Rev., **48**, 2008, p. 432.
3. BLOUIN, N., LECLERC, M., VERICELLI, B., ZECCHINI, S., ZOTTI, G., Macromol. Chem. Phys., **207**, 2006, p. 175.
4. LEVESQUE, I., BERTRAND, P.O., BLOUIN, N., LECLERC, M., ZECCHINI, S., ZOTTI, G., RATCLIFFE, C.I., KLUG, D.D., GAO, X., GAO, F., TSE, J.S., Chem. Mater., **19**, 2007, p. 2128.
5. KIRKUS, M., SIMOKAITIENE, J., GRAZULEVICIUS, J.V.; JANKAUSKAS, V., Synth. Met., **160**, 2010, p. 750.
6. VELASCOA, D., JANKAUSKAS, V., STUMBRAITE, J., GRAZULEVIVIUS, J.V., GETAUTIS, V., Synth. Met., **159**, 2009, p. 654.
7. LI, Y., WU, Y., GARDNER, S., ONG, B.S., Adv. Mater., **17**, 2005, p. 849.
8. WU, Y., LI, Y., GARDNER, S., ONG, B.S., J. Am. Chem. Soc., **127**, 2005, p. 614.
9. LI, Y., WU, Y., ONG, B.S., Macromolecules, **39**, 2006, p. 6521.
10. BOUDREAULT, P.L.T., WAKIM, S., BLOUIN, N., SIMARD, M., TESSIER, C., TAO, Y., LECLERC, M., J. Am. Chem. Soc., **129**, 2007, p. 9125.
11. TSAI, J.H., CHUEH, C.C., LAI, M.H., WANG, C.F., CHEN, W.C., KO, B.T., TING, C., Macromolecules, **42**, 2009, p. 1897.
12. BOUDREAULT, P.L.T., VIRKAR, A.A., BAO, Z., LECLERC, M., Org. Electron., **11**, 2010, p. 1649.
13. LEE, W.Y., CHEN, C.W., CHUEH, C.C., YANG, C.C., CHEN, W.C., Polym. J., **40**, 2008, p. 249.
14. LENGVINAITE, S., GRAZULEVICIUS, J.V., GRIGALEVICIUS, S., GUB, R., DEHAEN, W.,
JANKAUSKAS, V., ZHANG, B., XIE, Z., Dyes and Pigments, **85**, 2010, p. 183.
15. ZHAO, H.P., TAO, X.T., WANG, F.Z., REN, Y., SUN, X.Q., YANG, J.X., YAN, Y.X., ZOU, D.C., ZHAO, X., JIANG, M.H., Chem. Phys. Lett., **439**, 2007, p. 132.
16. HU, N., XIE, S., POPOVIC, Z.D., ONG, B., HOR, A., Synth. Met., **111-112**, 2000, p. 421.
17. ZHAO, H.P., WANG, F.Z., YUAN, C.X., TAO, X.T., SUN, J.L., ZOU, D.C., JIANG, M.H., Org. Electron., **10**, 2009, p. 925.
18. CHAN, L.H., LI, L.C., YAO, C.H., LIU, Y.R., JIANG, Z.J., CHO, T.Y., Thin Solid Films, **544**, 2013, p. 386.
19. LU, J., LIANG, F., DROLET, N., DING, J., TAO, Y., MOVILEANU, R., Chem. Commun., **44**, 2008, p. 5317.
20. CAI, S., TIAN, G., LI, X., SU, J., TIAN, H., J. Mater. Chem. A, **1**, 2013, p. 11295.
21. JANOSIK, T., WAHLSTROM, N., BERGMAN, J., Tetrahedron, **64**, 2008, p. 9159; BERGMAN, J., JANOSIK, T., WAHLSTROM, N., Adv. Heterocyclic Chem., **80**, 2001, p. 1.
22. KNOLKER, H.J., REDDY, K.R., Chem. Rev., **102**, 2002, p. 4303.
23. ROBINSON, B., J. Am. Chem. Soc., **85**, 1963, p. 3097.
24. THOLANDER, J., BERGMAN, J., Tetrahedron, **55**, 1999, p. 12577.
25. GU, R., HAMEURLAINE, A., DEHAEN, W., J. Org. Chem., **72**, 2007, p. 7207.
26. GU, R., HAUMERLAINE, A., DEHAEN, W., Synlett, **10**, 2006, p. 1535.
27. DEB, M.L., BHUYAN, P.J., Synlett, **3**, 2008, p. 325.
28. GU, R., SNICK, S., ROBEYNS, K., MEERVELT, L., DEHAEN, W., Org. Biomol. Chem., **7**, 2009, p. 380.
29. YUDINA, L.N., BERGMAN, J. S., Tetrahedron, **59**, 2003, p. 1265.
30. BLOUIN, N., MICHAUD, A., WAKIM, S., BOUDREAULT, P.L.T., LECLERC, M., VERCELLI, B., ZECCHINI, S., ZOTTI, G., Macromol. Chem. Phys., **207**, 2006, p. 166.
31. SNICK, S.V., DEHAEN, W., Org. Biomol. Chem., **10**, 2012, p. 79.

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