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Novel fluorescent stilbene analogs involving a carbazole moiety

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Abstract

The synthesis of a series of novel efficient TPA chromophores involving a carbazole moiety from *N*-(*p*-formyl)phenylcarbazole precursors and their linear absorption and fluorescent properties are described. © 2000 Published by Elsevier Science Ltd.

Recently, chromophores with a large two-photon absorption cross section have received much research interest due to their applications in multiphoton fluorescent imaging,[1] 3D optical data storage[2] and activation of photodynamic localized treatment.[3] Conjugated symmetrical analogs of *p*-diaminostilbene are known to possess pronounced two-photon absorption (TPA) properties.[4] Recently, we found that replacing the dialkylamino groups with a carbazole moiety gives rise not only to a further increase in the TPA coefficient δ, but also enhances the photostability of the resulting chromophores.[5] Here we report on the synthesis and fluorescence of these chromophores and their analogs.

The parent compound, 4,4′-bis(9-carbazolyl)stilbene **2a** has been previously synthesized in a low yield by the Ullmann reaction from 4,4′-dibromostilbene and carbazole.[6]

Our synthetic strategy is outlined in Scheme 1. It employs 9-(4′-formylphenyl)carbazole **1a** as the key precursor. Recently, this compound was also synthesized by Pd/P(t-Bu$_3$) catalyzed reaction of *p*-chlorobenzaldehyde with carbazole,[7] but no details were reported. Our approach involving Ullmann arylation of carbazole with *p*-bromo benzaldehyde[8] gave practically the same yields of **1a** as reported in Ref. 7, and is effective on a preparative scale also for the synthesis of other derivatives, such as **1b**.[9] The 3,6-dibromo derivative **1c** was obtained by direct bromination of **1a**.[10] Coupling of **1a** and **1c** by TiCl$_4$/Zn[11] in dry dioxane afforded stilbene derivatives **2a**,**c** in good yields.[10] Derivative **2b** was obtained by formylation of **2a** using the known procedure.[12]

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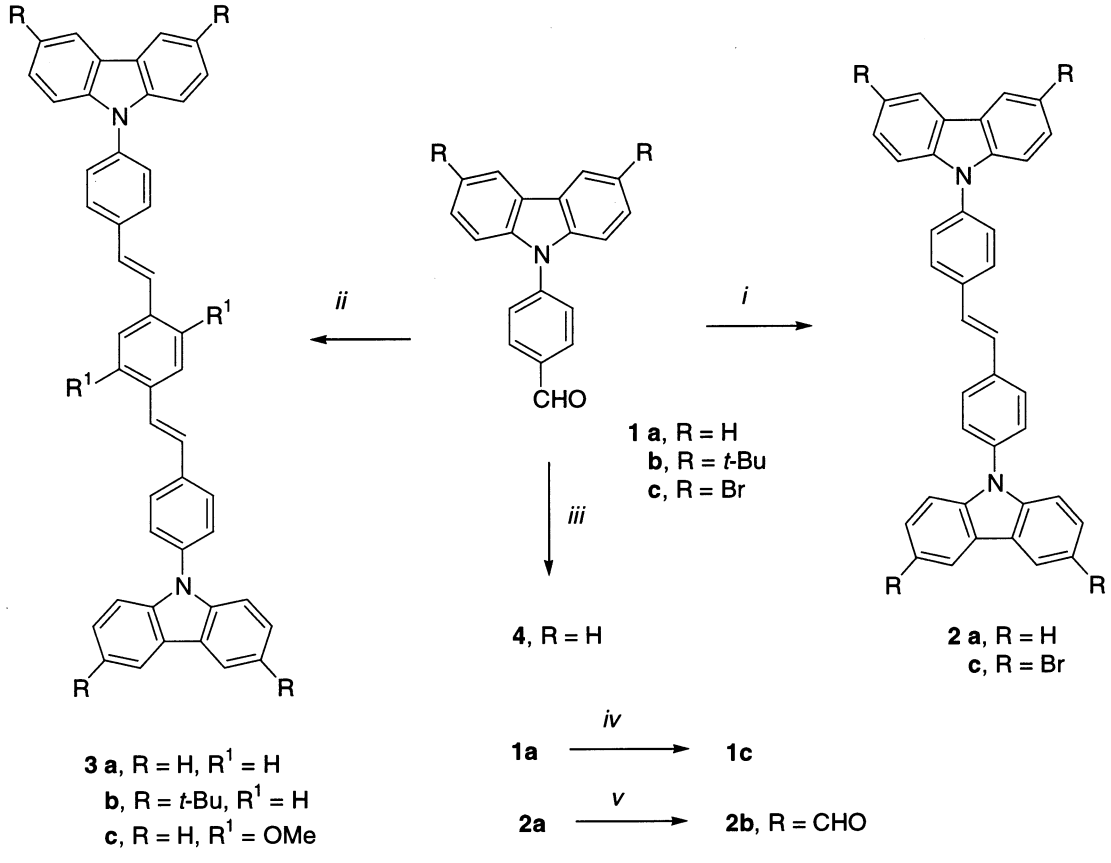
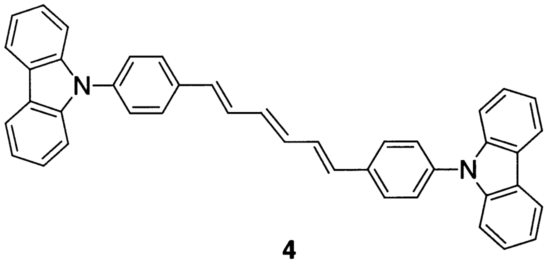


Scheme 1.



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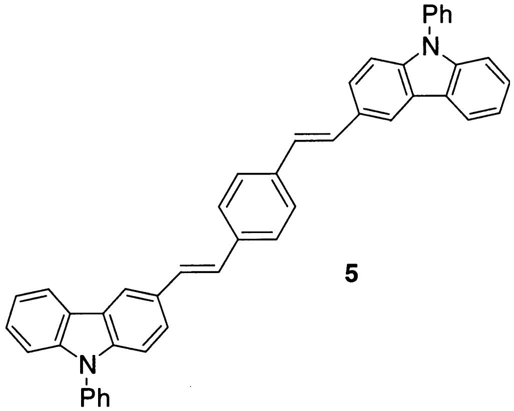

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Distyrylbenzene derivatives **3a**–**c** and diphenylhexatriene derivative **4** were synthesized by reacting **1** with the corresponding phosphonates in DMSO in the presence of *t*-BuOK.[10]

The crystal structure of **2a**[13] shows that the dihedral angle between the carbazole and stilbene moieties is 51.4° and, according to molecular modeling results, the fully planar conformation is sterically hindered.

For comparison, derivative **5**,[10] in which the carbazolyl moiety can be co-planar to the distyryl moiety, was synthesized from 3-formyl-*N*-phenyl carbazole by an analogous procedure.

Data on linear absorption and fluorescent properties of derivatives **2**–**5** are collated in Table 1. Interestingly, all chromophores that exhibit high fluorescence efficiencies (**3**, **4** and **5**), also possess the strongest TPA properties.[5] The photostability of **5**, in which the carbazolyl moiety can adopt the planar conformation, is noticeably lower than that of **3** and **4**. The presence of electron-accepting substituents in the carbazole moiety diminishes the fluorescence yield drastically. The fluorescence is also quenched in the presence of electron acceptors that can form charge transfer complexes with the carbazole moiety. Recently, we employed this effect for designing a system capable of reversible photo-induced emission switching.[14]

Table 1
Absorption, fluorescence and quantum yield of derivatives **2**–**5**

Compound	Solvent	λ_{abs} (nm)	λ_{em} (nm)	Quantum yield
2a	Toluene	348	397, 418	0.67
2b	Toluene	332, 343	395, 415	0.20
2c	Dichloromethane	344, 358	402, ~420	0.14
3a	Toluene	378	426, 448	0.70
3b	Toluene	406	458, 485	0.77
3c	Toluene	387	433, 439	0.87
4	Toluene	388	434, 459	0.68
5	Toluene	392	431, 457	0.92

Acknowledgements

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9. **1b**: A mixture of 1.15 g (4.12 mmol) of 3,6-di-*tert*-butylcarbazole,[15] 0.76 g (4.13 mmol) of 4-bromobenzaldehyde, 1.0 g of potassium carbonate, 0.05 g of Cu–bronze and 10 ml of nitrobenzene was boiled under reflux for 1 h and then the solvent was removed by steam distillation. The residue was extracted with hot petroleum ether (60–80°C) and the solid was crystallized from petroleum ether. Yield 0.7 g (44%), mp 111–112°C. ^{1}H NMR (200 MHz, $CDCl_3$): 10.10 (s, 1H, CHO), 8.18 (dd, 2H, $J=0.8$ Hz, 1.6 Hz, H-4,5), 8.11 (d, 2H, $J=8.6$ Hz, ArH), 7.79 (d, 2H, $J=8.6$ Hz, ArH), 7.44–7.55 (m, 4H, H-1,2,7,8), 1.40(s, 18H, CH_3); HRMS (CI): m/z (M+1) cac. fr $C_{27}H_{30}NO$ 384.2336, found 384.2327. **1c**: Yield 94%, mp 240–242°C; ^{1}H NMR (200 MHz, $CDCl_3$): 10.13 (s, 1H, CHO), 8.21 (d, 2H, $J=1.6$ Hz, H-4,5), 8.14 (d, 2H, $J=8.4$ Hz, ArH), 7.73 (d, 2H, $J=8.4$ Hz, ArH), 7.53 (dd, 2H, $J=1.6$, 8.7 Hz, H-2,7), 7.35 (d, 2H, $J=8.7$ Hz, H-1,8); HRMS (CI): m/z (M+1) cac. fr $C_{19}H_{12}Br_2NO$ 427.9285, found 427.9313.
10. **2a**: Yield 78%, mp 304–306°C. **2b**: Yield 46%, mp>300°C (decomp.). **2c**: Yield 65%, mp 419–420°C (decomp.). **3a**: Yield 40%, mp 338°C. **3b**: Yield 43%, mp 356°C. **3c**: Yield 7.4%, mp 318–320°C. **4**: Yield 6%, mp 248–250°C. **5**: Yield 13%, mp 268°C. The structure of these compounds was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS spectra.
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13. X-ray analysis of **2a**: A colorless prism (0.5×0.3×0.3 mm) of $C_{38}H_{26}N_2$ was used for X-ray intensity data measurements on a standard Bruker SMART CCD 1000™ diffractometer (λ(Mo Kα) = 0.71073 Å, graphite monochromator, a scan width of 0.3° in ω and an exposure time of 10 s/frame, detector-crystal distance 5.05 cm). A total of 1080 frames were collected and integrated with Bruker SAINT software package using a wide-frame integration algorithm. The crystal is monoclinic, space group $C2/c$, at 298 K, $a=24.77(1)$, $b=9.8395(5)$, $c=12.3545(7)$, $\beta=117.873(3)°$, $Z=4$, $V=2662.5(2)$ Å^3, $F(000)=1072$. 17 844 reflections were collected ($2\theta<41.62°$), of which 1507 reflections were independent ($R_{int}=14.00\%$) and 1396 with $F_o>4\sigma(F_o)$. Data were corrected for absorption using the SADABS program.

    The structure was solved by direct methods and refined by least-squares in the full-matrix approximation: 182 parameters, $R_1=5.26\%$, $wR_2=15.21\%$, GOF = 1.073. The Bruker SHELX software package was used for all calculations.
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