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Mechanical Strain Sensing in a SIS-Type Elastomer with Single Site Strain Probes Based on Carbazole

Holger Spanggaard,* Mikkel Jørgensen, and Kristoffer Almdal

The Danish Polymer Centre, RISØ National Laboratory, P.O. Box 49, DK-4000 Roskilde, Denmark

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ABSTRACT: Four fluorescent strain probes with one or two carbazole units placed in the middle of an elastomeric triblock of polystyrene−polyisoprene−polystyrene (SIS) have been prepared and their fluorescence behaviors investigated under strain. The probes were dissolved in commercial SIS type rubbers at low levels of 0.1 wt %. Films cast from this blend were subjected to tensile elongation while the fluorescence spectra were obtained. A rather large change from ca. 0.7 to 1.1 in the relative intensity at two wavelengths (I_{350}/I_{370}) was observed on elongations up to 400%. The spectroscopic change is strongest for small strain levels around 0−200% and leveled out above 300−400%. This is attributed to changes in the intensities of the vibronic bands of the substituted carbazole units rather than changes in molecular overlap of carbazole dimers.

Introduction

Poly(*N*-vinylcarbazole) (PVCz) has been advanced as a fluorescent probe material for measuring residual strain in polymer matrices.[1] The working principle in this material is the difference in fluorescence intensities obtained at two different wavelengths (345 and 375 nm) as a function of strain. In the PVCz polymer, the carbazole units are connected to the main chain at every second carbon atom. The fluorescence properties of such carbazole dimers have been investigated in some detail by De Schryver et al.[2] Several types of overlap between neighboring carbazoles are possible that can be recognized as giving rise to different fluorescence maxima. PVCz is, however, not an ideal material in several respects. First, it is rather brittle and only modest strain values of less than 1% were attained. Second, each PVCz chain gives rise to very many differently overlapping carbazoles. The fluorescence detected is therefore an average not only between chains, but also within a chain. It would therefore seem valuable to investigate simpler systems with only one or two carbazole units placed in a polymer chain (and also much more synthetically challenging). Changes in fluorescence as a function of tensile elongation should be easier to interpret. It would also be possible to choose a polymer material that could be strained much more.

Results and Discussion

In the present work, we have prepared and investigated four different single-site probes based on the carbazole fluorophore. Two diblock polystyrene−polyisoprene (PS−PI) units were linked to either one carbazole group through the 3 and 6 positions (probe **1**) or to the 3 and 3′ positions of a carbazole dimer (probes **2**, **3**, and **4**). In the latter cases, propyl groups were used to bridge the carbazole units via the nitrogen atoms. (See Figure 1.)

A polystyrene−polyisoprene−polystyrene triblock copolymer (SIS) was chosen as a matrix for the carbazole unit because it is an elastomer that can be stretched by a factor of more than 10. The microstructure of the SIS elastomers is well-known.[3] If the styrene component is less than 30 wt %, the two blocks separate to form PS domains of spherical symmetry surrounded by a matrix of interconnecting PI chains. When this material is stretched, the PS domains behave as rigid bodies and most of the strain develops in the PI blocks. Dispersing the labeled polymer in a low concentration (0.1 wt %) should have little effect on the overall microstructure as shown in Figure 2. Different commercial types of SIS elastomers differing in molar mass and composition have been used in this study.

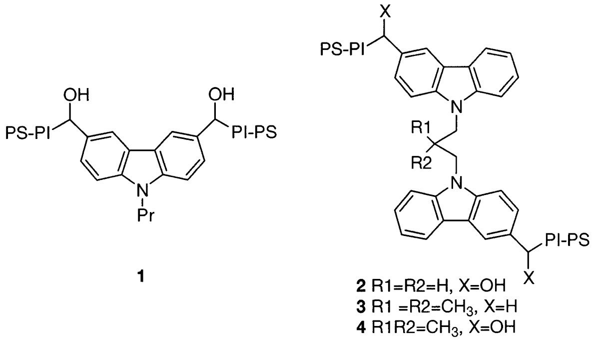

Figure 1. Single site probes used in this study, with one or two carbazole units linked to PS−PI elastomer groups.

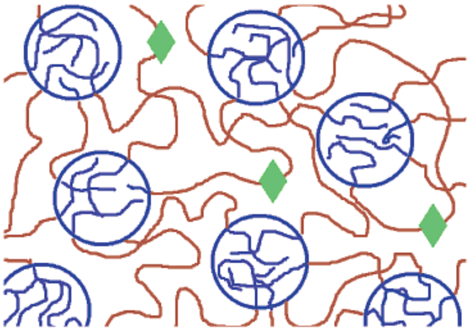

Figure 2. Microstructure of the prepared triblocks. The blue spheres are the PS domains, the PI domain is orange, and the green diamonds symbolize the fluorescent carbazole groups.

Synthesis. The synthesis of probe **1** was carried out as shown in Scheme 1. *N*-Propyl-3,6-dibromocarbazole[4] was converted into the corresponding dialdehyde **5** by bromine-to-lithium exchange with *tert*-butyllithium in

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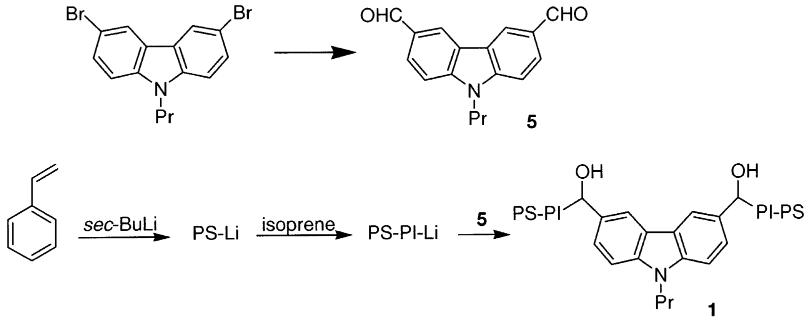
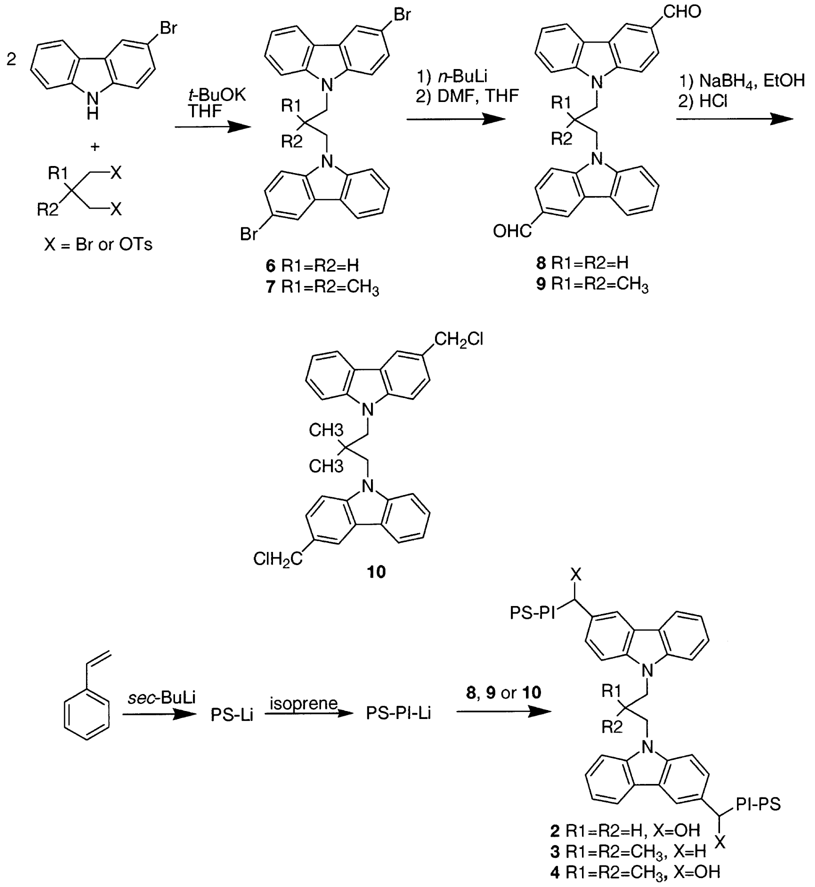
Scheme 1. Synthesis of Probe 1



Scheme 2. Synthesis of Probes 2, 3, and 4



dry tetrahydrofuran followed by reaction with dimethylformamide.

Synthesis of the polystyrene−polyisoprene (PS−PI) block copolymer units and their attachment to the sensor unit is outlined in Scheme 2. Anionic living polymerization of styrene followed by polymerization of isoprene was carried out under inert atmosphere[5] to give a PS−PI−Li diblock (19 wt % styrene and 81 wt % isoprene and total a weight of 75 kg/mol). The 3,6-diformyl-9-propylcarbazole **5** was then added to the reaction mixture in less than an equivalent amount in order to ensure complete conversion to the desired single site sensor molecule **1**. It was found advantageous to add tetrahydrofuran at this step as a cosolvent to augment the relatively weak nucleophilicity of the lithiated polymer, as also noted by Hirao et al.[6] Purification by repeated precipitation from chloroform-methanol gave compound **1** mixed with some unreacted PS−PI diblock. Coupling of two PS−PI blocks to compound **3** approximately doubles the molar mass, which was conveniently followed by SEC. The purified single site sensor compound was found to have a molar mass of 150 kg/mol with a dispersion (M_w/M_n) of 1.2.

Syntheses of the probes **2**, **3**, and **4** are outlined in Scheme 2. 2,2-Dimethyl-1,3-propanediols were reacted with *p*-tolenesulfonyl chloride to prepare the corresponding reactive tosyl esters.[7] This tosylate and 1,3-dibromopropane were used to alkylate 3-bromocarbazole[8] to prepare the carbazole dimers **6** and **7** bridged by propyl units, either unsubstituted or with two methyl groups in the 2-position. Bromine-to-lithium exchange followed by reaction with dimethylformamide gave the aldehyde substituted bis(carbazoles) **8** and **9**. The aldehyde groups were reduced with sodium borohydride to the benzylic alcohols that were transformed into the corresponding chloromethyl derivative **10.** Anionic polymerization of styrene followed by isoprene was used as in the preparation of probe **1** to create the diblocks that was then used in a final step to prepare the probes **2**, **3**, and **4**.

Fluorescence Properties of the Strain Probes in Solution. The fluorescence spectra of the chromophore

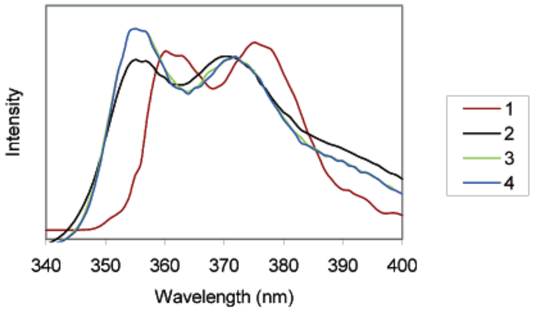


Figure 3. Emission spectra of **1**, **2**, **3**, and **4** dissolved in chloroform (the traces for **3** and **4** are almost superimposed). Excitation wavelength is 310 nm.

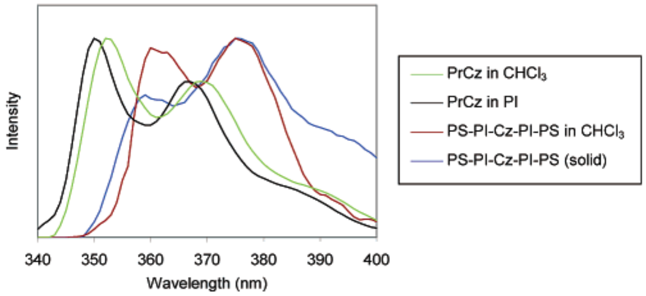


Figure 4. Emission spectra of carbazole with or without polymer substituents in the 3- and 6-positions in chloroform or in PI surroundings. In all cases, carbazole was *N*-substituted with propyl. The spectra have been normalized with respect to maximum intensity. Excitation wavelength is 310 nm.

units of the four strain probes were measured in chloroform (see Figure 3). The bis(carbazole) systems **2**, **3**, and **4** have similar spectra while the spectrum of **1** is red-shifted around 6 nm. This is an effect of the two substituents on carbazole in **1** compared to one substituent on each carbazole in **2**, **3**, and **4**.

It was verified by preparation and comparison of the emission spectra of *N*-propylcarbazole, *N*-propyl-3-methylcarbazole, and *N*-propyl-3,6-dimethylcarbazole which show a progressive red-shift with increased substitution. Solvent polarity on the other hand did not change the spectra of the strain probes more than 1−2 nm in the series: *n*-heptane, toluene, chloroform, dichloromethane, or ethanol.

The effect of viscosity on the spectrum of *N*-ethylcarbazole was studied by comparing the emission spectra in chloroform (see Figure 4) and low molecular weight 1,4-*cis*-polyisoprene (MW = 20 kg/mol), showing only a minor blueshift of 2−3 nm in the more viscous polymer medium.

No evidence of full overlap excimer type fluorescence from the bis(carbazoles) (**2**, **3**, and **4**) was found, which should have been clearly visible as a strong peak centered around 420 nm. This is in contrast with the results found by Vandendriessche et al. for the closely related *rac*- and *meso*-2,4-di(*N*-carbazolyl)pentanes, where evidence for partial and complete overlap between the carbazole moieties were found. It must be concluded that the structures with partial or total overlap only occurs in very special circumstances found in the two pentane derivatives. These findings also have an impact on the interpretation of the fluorescence spectra of PCBz used by Ikawa et al. and the probes imbedded in SIS rubber used in this study.

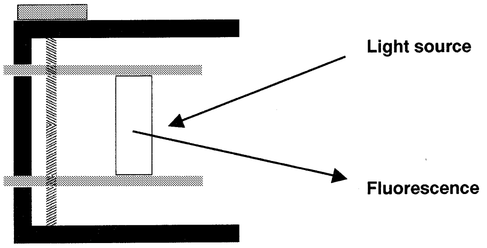


Figure 5. Jig for uniaxial elongation of the rubber films mixed with strain probes **1**, **2**, **3**, and **4**.

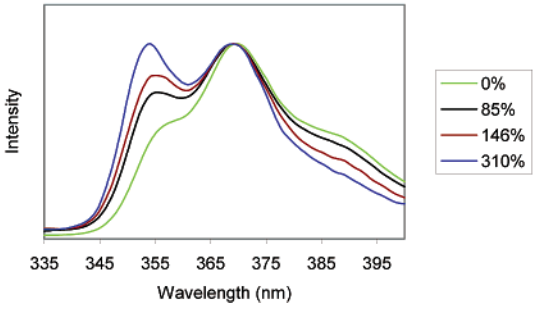


Figure 6. Representative normalized spectra at varying strain of **2** dissolved in a commercial SIS elastomer.

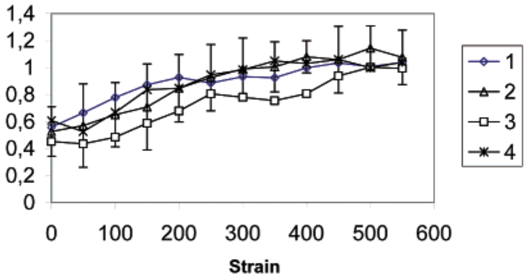


Figure 7. I_{352}/I_{370} (I_{357}/I_{375} for **1**) as a function of strain. Each data point is the average of 10 measurements. For clarity, error bars (standard deviations) are only shown for **2**.

Fluorescence Properties of the Strain Probes in Elastomer Films. Films of the strain probes were obtained by mixing 0.1 wt % (corresponding to ca. 10^{-5} M in carbazole) of **1**, **2**, **3**, or **4** in a solution of a SIS elastomer in chloroform. The solutions were poured into Petri dishes and the solvent was allowed to evaporate slowly over 24 h. to give homogeneous transparent films of 1−2 mm thickness. Strips 10 mm wide and 30 mm long were then cut from the film and mounted in a jig for uniaxial elongation (see Figure 5).

The test apparatus was then placed in the sample bay of a fluorescence spectrometer with the film oriented for back face measurement. This arrangement, recommended by Itagaki et al.,[9] ensures that the detected light is not the result of reflection or a possible surface phenomenon. We found that most consistent data were obtained by illuminating a relatively large area (>4−5 mm^2) to average local variations. The optical density was kept below 0.05 in the emitting region to prevent reabsorption.

In Figure 6, normalized spectra of **2** dissolved in a commercial SIS elastomer is shown as the film is progressively stretched. As can be seen the intensity around 352 nm is increasing as the film is strained.

1, **2**, **3**, and **4** all displayed the same behavior upon strain, except that the spectrum of **1** was red-shifted by 5−7 nm as expected from the spectrum in chloroform. Plotting the intensity ratio I_{352}/I_{370} (I_{357}/I_{375} for **1**) as a function of strain results in Figure 7. The effect of strain is largest for small values of strain (0−200%) and then the ratio levels out to about 1.05 at strain levels of 300−400% and above. Though clear trends were observed for every data series, there were large deviations between the series and this is reflected in relatively large error bars.

All four strain probes gave similar results on uniaxial elongation. It is somewhat surprising that probe **1** with only one carbazole unit should give the same results as the biscarbazole probes **2**, **3**, and **4**. This rules out any major contribution from excimer to monomer type shifts in the fluorescence of the latter probes, which is in accordance with the absence of an emission peak centered around 420 nm, ascribed to the excimer. Large changes in the relative intensities of the monomer emission bands are on the other hand related to the strain. A possible explanation could involve a progressive orientation of the carbazole units as the film was stretched. Unfortunately, it proved impossible to test this hypothesis using the polarization of light to measure orientation.[10] The samples are sufficiently opaque that the polarization is lost from multiple scattering.

An important question is whether the change is caused by the immediate surroundings of the carbazole or the change is a mechanical effect of the stretching of the polymer chains connecting carbazole to the network. To answer this question, a polymer consisting of PI with a carbazole unit in the middle was prepared in a similar manner as outlined in Scheme 2, but the polymer chain was not a PS−PI diblock but only PI. Here, 0.1 wt % of the prepared polymer was mixed with a commercial PS−PI−PS triblock. Repeating the strain experiment showed no effect on the emission spectrum of strain. This strongly indicates that polymer chains on carbazole must be connected to the network if straining of the sample is to produce any effect on the emission spectrum. The result is interesting from a theoretical point of view: the theory of rubber elasticity states that the force required when stretching rubber is primary entropic in origin for small strains. Thus, there is no (or little) force transmitted through the polymer chains. However, at the high strains applied in the current study, the emission spectrum of carbazole depends on whether the PI chain is linked to the PS domains or not, indicating that the fluorescence properties of carbazole is sensitive to the little amount of force transmitted through the chains.

Conclusion

Four different strain probes with one or two carbazole units placed in the middle of a SIS type triblock copolymer has been prepared. Fluorescence spectra of the chromophores in solution are remarkably similar and all show fluorescence expected for a simple monomeric carbazole type chromophore. This is in contrast to the very similar 2,4-(*N*-carbazolyl)pentanes studied by Vandendriessche et al. were evidence for partial and total overlap between the carbazole units were seen in the eximer type spectra obtained. Strain probes **1**−**4** were mixed in commercial SIS rubber at the 0.1% level and made into film strips. When these films were subjected to uniaxial elongation large changes from 0.7 to 1.1 in the relative fluorescence intensities at two wavelengths (350 and 370 nm) was nonetheless observed. The change was largest for strains around 0−200% and leveled out above 300−400%. Since the results are similar for the mono- and bis(carbazole) probes changes in molecular overlap giving rise to eximer type fluorescence can be excluded. The observed changes must instead be due to subtle changes in the transition probabilities of the vibronic bands of the carbazole units. This finding casts doubts on the interpretation by Ikawa et al. on fluorescence spectra on stretched PVCz films. It was assumed that the changes observed were related to the different ratios of overlap geometries in response to the induced strain. While this may still be the case it cannot be excluded that the variations observed was instead related to fluorescence changes in the monomer carbazole units themselves, as in our case. The preparation of single chromophoric units imbedded in the polymer matrix proved to be crucial in separating the factors responsible for the fluorescence changes. These strain probes may also be more generally valuable since they can be used with a larger selection of polymer matrices.

Experimental Section

Photophysical Methods. All fluorescent measurements were carried out on a standard FLS920 from Edinbugh Instruments, with a 450 W Xe lamp for steady-state measurements and a nanosecond flash lamp for time-resolved measurements. The detecting system comprises a single photon counting PMT detector in a peltier cooled housing. All spectra where obtained using a backface arrangement. All emission spectra where obtained by exciting at 310 nm, using a 1 s acquisition time at each nanometer increment, and corrected with a 1.8 nm band-pass.

3,6-Diformyl-*N*-propylcarbazole (5). 3,6-Dibromo-*N*-propylcarbazole (2.0 g; 5.4 mmol) was dissolved in dry THF (250 mL). The solution was cooled to −78 °C and *t*-BuLi (27 mmol) was added. The temperature was allowed to rise to 0 °C. The solution was recooled to −78 °C and dry DMF (8 g; 100 mmol) was added. The temperature was allowed to rise to RT. After 30 min, HCl(aq) was added, the volume was reduced in vacuo, and the precipitate was filtered. Recrystallization from ethanol afforded the product in 43% yield (0.62 g; 2.3 mmol). Mp: 142−144 °C. ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.9$ (t, $J = 7.4$ Hz, 3H, $-CH_3$), 1.8 (m, 2H), 4.5(d, $J = 7.1$ Hz, 2H), 7.9(d, $J = 8.6$ Hz, 2H), 8.1(d, $J = 8.6$ Hz, 2H), 8.9(s, 2H), 10.1(s, 2H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6): $\delta = 11.1$, 21.7, 44.3, 110.6, 122.3, 124.3, 127.2, 129.2, 144.4, 191.8 ppm. Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.76; H, 5.74; N, 5.18.

1,3-bis(3-bromocarbazole-9-yl)propane (6). 3-Bromocarbazole (15.5 g; 63.3 mmol) was dissolved in dry THF (350 mL), and LDA (70 mmol) was added. After 5 min, 1,3-dibromopropane (7.65 g; 37.9 mmol) was added and the mixture was refluxed overnight. Water was added, and the solution was extracted with ether (2 × 200 mL). The organic phase was dried ($MgSO_4$), and the solvent was removed in vacuo. Recrystallization from toluene/heptane gave the product as a white powder in 61% yield. Mp: 181−183 °C. ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 2.2$ (m, 2H), 4.5 (t, $J = 7.2$ Hz 4H), 7.2 (t, $J = 5.8$ Hz, 2H), 7.5 (m, 8H), 8.2 (d, $J = 8.2$ Hz, 2H), 8.4 (s, 2H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6): $\delta = 27.5$, 109.2, 110.9, 119.2, 120.8, 121.1, 122.8, 124.0, 126.4, 127.9, 138.5, 149.1 ppm (one aliphatic peak and one aromatic peak are missing). Anal. Calcd. for $C_{27}H_{20}N_2Br_2$: C, 60.93; H, 3.79; N, 5.26. Found: C, 60.89; H, 3.81; N, 5.24.

1,3-bis(3-formylcarbazole-9-yl)propane (8). 1,3-bis(3-bromocarbazole-9-yl)propane (2.43 g; 4.57 mmol) was dissolved in dry THF. The solution was cooled to −78 °C and treated with *n*-BuLi (16 mmol). After 5 min, dry DMF (3.3 g; 45 mmol) was added and the temperature was allowed to rise to room temperature. After 30 min, HCl(aq) was added, the volume was reduced in vacuo and the precipitate was filtered. Recrystallization from ethanol afforded the product in 59% yield (1.16 g; 2.7 mmol). Mp: 243−245 °C. ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 2.3$ (m, 2H), 4.6 (t, $J = 7$ Hz, 4H), 7.3 (t, $J = 7$ Hz, 2H), 7.5 (t, $J = 8$ Hz, 8H), 7.6 (d, $J = 8$ Hz, 2H), 7.7 (d, $J = 8$

Hz, 2H), 7.9 (d, *J* = 8 Hz, 2H), 8.3 (d, *J* = 8 Hz, 2H), 8.7 (s, 2H), 10.0 (s, 2H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6): δ = 27.3, 109.5, 109.7, 120.2, 120.8, 122.3, 123.9, 126.6, 126.7, 128.4, 140.5, 143.3, 191.7 ppm (one aliphatic peak and one aromatic peak are missing). Anal. Calcd. for $C_{29}H_{22}N_2O_2$: C, 80.91; H, 5.15; N, 6.51. Found: C, 81.13; H, 5.20; N, 6.59.

1,3-Bis(3-bromocarbazole-9-yl)-2,2-dimethylpropane (7). 3-bromocarbazole (21.9 g; 89.0 mmol) was dissolved in dry DMF (400 mL) and treated with potassium *tert*-butoxide (14.4 g; 129 mmol). After 10 min, 1,3-ditosyl-2,2-dimethylpropane (18.8 g; 45.6 mmol) was added. The dark mixture was stirred at 120 °C for 20 h, and water was added. The precipitate, a white powder, was washed with hot ethanol yielding the product sufficiently pure for further reaction. Yield: 52% (12.9 g; 23.1 mmol). Mp: 207−208 °C. ^{1}H NMR (250 MHz, DMSO-d_6): δ = 1.0 (s, 6H), 4.6 (s, 4H), 7.2 (t, *J* = 8 Hz, 2H), 7.5 (t, *J* = 8 Hz, 2H), 7.6 (d, *J* = 9 Hz, 2H), 7.7 (d, *J* = 4 Hz, 2H), 7.8 (d, *J* = 4 Hz, 2H), 8.2 (d, *J* = 8 Hz, 2H), 8.4 (s, 2H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6): δ = 25.3, 43.7, 51.2, 110.8, 111.0, 112.6, 119.3, 120.6, 121.2, 122.6, 124.2, 126.3, 127.8, 140.2, 141.8 ppm. Anal. Calcd. for $C_{29}H_{24}Br_2N_2$: C, 62.16; H, 4.32; N, 5.00. Found: C, 62.37; H, 4.23; N, 4.87.

1,3-Bis(3-formylcarbazole-9-yl)-2,2-dimethylpropane (9). 1,3-Bis(3-bromocarbazole-9-yl)-2,2-dimethylpropane (1.97 g; 3.52 mmol) was dissolved in dry THF (150 mL) and treated with *t*-BuLi (11 mL of a 1.7 M solution in hexane, 18.7 mmol) at −78 °C. The temperature was allowed to rise to 0 °C and then cooled to −78 °C. Excess dry DMF (3 g; 41 mmol) was added, and the temperature was allowed to rise to room temperature. After 30 min, HCl(aq) was added, and the volume was reduced in vacuo. The precipitate was collected and recrystallized from toluene/heptane leaving the product as a yellow powder. Yield: 56% (0.90 g; 2.0 mmol). Mp: 232−234 °C. ^{1}H NMR (250 MHz, DMSO-d_6): δ = 1.0 (s, 6H), 4.7 (s, 4H), 7.3 (t, *J* = 7 Hz, 2H), 7.5 (t, *J* = 7 Hz, 2H), 7.9 (d, *J* = 8 Hz, 2H), 8.0 (s, 4H), 8.3 (d, *J* = 8 Hz, 2H), 8.8 (s, 2H), 10.1 (s, 2H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6): δ = 25.3, 43.6, 51.2, 111.2, 111.4, 120.2, 120.6, 122.4, 122.5, 123.7, 126.3, 126.5, 128.4, 142.3, 145.0, 191.8 ppm. Anal. Calcd. for $C_{31}H_{26}N_2O_2$: C, 81.20; H, 5.72; N, 6.11. Found: C, 80.91; H, 5.86; N, 5.90.

1,3-Bis(3-hydroxymethylcarbazole-9-yl)-2,2-dimethylpropane. A mixture of 1,3-bis(3-formylcarbazole-9-yl)-2,2-dimethylpropane (230 mg; 0.50 mmol) and excess $NaBH_4$ (80 mg; 2.1 mmol) was stirred in THF−ethanol (15 mL:15 mL) for 6 h at room temperature. The volume was reduced in vacuo and poured into water. The white precipitate was collected and dried, affording the product sufficiently pure for further reaction. Analytical pure product could be obtained by recrystallization from ethanol/toluene. Yield: 86% (0.20 g; 0.43 mmol). Mp: 189−191 °C. ^{1}H NMR (250 MHz, DMSO-d_6): δ = 1.1 (s, 6H), 4.6 (s, 4H), 4.7 (s, 4H), 5.2 (br, 2H), 7.2 (t, *J* = 7 Hz, 2H), 7.4 (t, *J* = 8 Hz, 2H), 7.4 (t, *J* = 8 Hz, 2H), 7.7 (d, *J* = 6 Hz, 4H), 7.7 (d, *J* = 6 Hz, 2H), 8.1 (s, 2H), 8.2 (d, *J* = 8 Hz, 2H). ^{13}C NMR (63 MHz, DMSO-d_6): δ = 25.5, 43.8, 51.3, 63.5, 110.1, 110.5, 118.2, 118.8, 119.9, 122.0, 122.2, 124.9, 125.3, 133.2, 140.7, 141.8 ppm. Anal. Calcd. for $C_{31}H_{30}N_2O_2$: C, 80.49; H, 6.54; N, 6.06. Found: C, 80.49; H, 5.76; N, 5.94.

1,3-Bis(3-chloromethylcarbazole-9-yl)-2,2-dimethylpropane (10). 1,3-Bis(3-hydroxymethylcarbazole-9-yl)-2,2-dimethylpropane (0.30 g; 0.65 mmol) was dissolved in chloroform (75 mL). Concentrated hydrochloric acid (25 mL) was added, and the mixture was vigorously stirred at 0 °C. After 30 min, the phases were separated. The organic layer was successively washed with water, $NaHCO_3$(aq), and water and then dried ($MgSO_4$). The solvent was removed in vacuo leaving the product as a yellow glass in 83% yield (0.26 g; 0.54 mmol). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 1.0 (s, 6H), 4.6 (s, 4H), 5.0 (s, 4H), 7.2 (t, *J* = 7 Hz, 2H), 7.5 (t, *J* = 8 Hz, 2H), 7.5 (t, *J* = 9 Hz, 2H), 7.8 (d, *J* = 8 Hz, 2H), 7.8 (d, *J* = 8 Hz, 2H), 8.2 (d, *J* = 8 Hz, 2H), 8.3 (s, 2H). ^{13}C NMR (63 MHz, DMSO-d_6): δ = 25.4, 43.6, 47.5, 51.3, 79.1, 110.7, 119.1, 120.0, 120.8, 122.0, 122.2, 125.7, 126,7. 128.1, 141.3, 141.9 ppm. Anal. Calcd. for $C_{31}H_{28}Cl_2N_2 \cdot 0.3HCl$: C, 72.95; H, 5.59; N, 5.49. Found: C, 72.88; H, 5.58; N, 5.38.

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