# **Supporting Information**

## Luminescent Diazaborolyl-Functionalized Polystyrene

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#### **Experimental Section**

**Materials and Methods.** BBr<sub>3</sub> (99.9%) was purchased from Acros and used as received. **Caution!** *BBr<sub>3</sub> is toxic and highly corrosive and should be handled appropriately with great care.* Fluorinated grease was used for ground glass joints in all reactions involving boron tribromide. Poly(4-trimethylsilyl styrene) (1) of  $M_n = 56,300$ ;  $M_w = 65,200$ ; *PDI* = 1.16 (GPC-RI) /  $M_n = 69,000$ ;  $M_w = 78,700$ ; *PDI* = 1.14 (GPC-MALLS) and N,N'-diethyl-1,2-phenylendiamine and N,N'-diphenyl-1,2-phenylendiamine were synthesized as previously reported.<sup>[11]</sup> All reactions were carried out under inert atmosphere using Schlenk techniques or a glove box (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. The chlorinated solvents were distilled from CaH<sub>2</sub> and degassed via several freeze-pump-thaw cycles.

**Instrumentation.** The 500.1 MHz <sup>1</sup>H NMR and 125.75 MHz <sup>13</sup>C NMR spectra were recorded on a Bruker AM Acance DRX 500 or a a Varian INOVA spectrometer and referenced internally to solvent signals. The 160.4 MHz <sup>11</sup>B NMR spectra were acquired on a Varian INOVA spectrometer equipped with a boron-free 5 mm dual broadband gradient probe using boron-free quartz NMR tubes and referenced externally to BF<sub>3</sub> · Et<sub>2</sub>O ( $\delta = 0$ ). All NMR spectra were recorded at ambient temperature unless noted otherwise.

**Polymer Characterization**. Gel permeation chromatography (GPC) analyses (THF, 1 mL min<sup>-1</sup>) were performed using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2998 photodiode array detector, and a 2414 refractive index detector. A series of styragel columns (Polymer Laboratories; two 5  $\mu$ m Mix-C columns in series), which were kept in a column heater at 35 °C, were used for separation. The columns were calibrated with a set of 10 narrow PS standards (Polymer Laboratories). The triple detection GPC measurement was performed in THF (1 mL min<sup>-1</sup>) at 65 °C with the same column set using a Viscotek TDA305 Max Triple Detection SEC system by Malvern. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Pyris 1 system with ca. 8 mg of polymer using a scan rate of 20 °C/min from 25 °C to 300 °C. Thermogravimetric analyses (TGA) were a heating rate of 10 °C/min from 30 to 800 °C. The elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

**Photophysical measurements**. For all solution state measurements, samples were contained in quartz cuvettes of 10 × 10 mm (Hellma type 111-QS, suprasil, optical precision). All solvents were dried by standard methods prior to use. Concentrations varied from 10 to 50  $\mu$ M according to their optical density. The absorption was measured with a UV/VIS double-beam spectrometer (Shimadzu UV-2550), using the solvent as a reference. The setup used to acquire excitationemission spectra (EES) was similar to that employed in commercial static fluorimeters: The output of a continuous Xe-lamp (75 W, LOT Oriel) was wavelength-separated by a first monochromator (Spectra Pro ARC-175, 1800 l/mm grating, Blaze 250 nm) and then used to irradiate the sample. The fluorescence was collected by mirror optics at right angles and imaged on the entrance slit of a second spectrometer while compensating astigmatism at the same time. The signal was detected by a back-thinned CCD camera (RoperScientific, 1024 \ 256 pixels) in the exit plane of the spectrometer. The resulting images were spatially and spectrally resolved. As the next step, one averaged fluorescence spectrum was calculated from the raw images and stored in the computer. This process was repeated for different excitation wavelengths. The result is a two-dimensional fluorescence pattern with the y-axis corresponding to the excitation, and the *x*-axis to the emission wavelength. A sample spectrum obtained with this technique is shown. Here, the wavelength range is  $\lambda_{ex} = 200-400$  nm (in 1 nm increments) for the UV light and  $\lambda_{em} = 210-800$  nm for the detector. The time to acquire a complete EES is typically less than 15 min. Post-processing of the EES includes subtraction of the dark current background, conversion of pixel to wavelength scales, and multiplication with a reference file to take the varying lamp intensity as well as grating and detection efficiency into account. The quantum yields in solution were determined against POPOP (*p*-bis-5-phenyl-oxazolyl(2)-benzene) ( $\Phi = 0.93$ )



Sample EES spectrum of **3b** in  $CH_2Cl_2$  solution

as the standard. The lifetime measurements in solution where performed with a time-resolved LIF (laser induced fluorescence) setup, equipped with a Ti: sapphire-Laser, pulse frequency of 80 ps and effective excitation at 297 nm. Solutions of 50  $\mu$ M concentration in CH<sub>2</sub>Cl<sub>2</sub> were used. More information about this setup, as well as further measurement conditions for lifetime studies, have been reported previously.<sup>[2]</sup>

A polymer film was prepared by dropping a concentrated  $CH_2Cl_2$  solution of **3b** onto a quartz slide and slowly evaporating the solvent under Argon at room temperature. The solid-state quantum yield was measured by addition of an integrating sphere (Labsphere, coated with Spectralon, Ø 12.5 cm) to the existing experimental setup. The excitation light was transferred into a quartz fiber (LOT Oriel, LLB592) at the exit slit of the first monochromator. The light passed a condenser lens and illuminated a 1 cm<sup>2</sup> area on the sample in the centre of the sphere. The emission and exciting light was imaged by a second quartz fiber on the entrance slit of the detection monochromator. The optics for correction of astigmatism was passed by the light on its way. Post processing of the spectra was done in the same way as described above. The measurement and calculation of quantum yields was performed according to the method described by Mello.<sup>[3]</sup>

The luminescence lifetime for the thin film was measured with a time-correlated single-photon counting apparatus (TCSPC, Horiba Jobin Yvon FluoroHub, light source: Nano-LED280, detector: Photomultiplier TBX). The excitation wavelength was separated by using an edge filter in front of the detection.

Synthesis of Polymer 3a. Procedure 1. In a glovebox, a solution of poly(4-trimethylsilyl styrene) (1, 930 mg, 5.21 mmol SiMe<sub>3</sub> groups) in 20 mL CH<sub>2</sub>Cl<sub>2</sub> was added to a precooled (-35 °C) solution of BBr<sub>3</sub> (1.54 g, 6.15 mmol, 1.1 equiv) in 20 mL CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred under a nitrogen atmosphere for 24 h. A solution containing N, N'-diethyl-1,2-diaminobenzene (1.01 g, 6.15 mmol) and triethylamine (1.32 g, 13.0 mmol, 2.1 equiv) in 30 mL CH<sub>2</sub>Cl<sub>2</sub> was cooled to -35 °C and slowly added via syringe. The resulting mixture was stirred in the glove box overnight. During the addition some precipitation occurred, but the solid eventually redissolved. The yellowish solution was partially evaporated and then slowly added to a 10-fold volume of hexanes to precipitate the polymer. The white precipitate was allowed to settle, the supernatant was decanted via syringe, and the solid was washed twice with hexanes. The solid was redissolved in benzene, stirred for 24 h, and then allowed to settle. The solution was decanted, filtered through celite<sup>®</sup> and then freeze-dried in vacuum. The crude product was further purified by dissolution in benzene, centrifugation for 30 min at 5.000 rpm, decantation, and freeze-drying in vacuum. The product is obtained as a white powder (590 mg, 35 %).

**Procedure 2.** In a glovebox, a solution of poly(4-trimethylsilyl styrene) (1, 500 mg, 2.80 mmol SiMe<sub>3</sub> groups) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was added to a precooled (-35 °C) solution of BBr<sub>3</sub> (773 mg, 3.08 mmol, 1.1 equiv) in 10 mL CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred in the glovebox for 24 h. A solution of N,N'-diethyl-1,2-diaminobenzene (920 mg, 5.60 mmol, 2.0 equiv) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was cooled to -35 °C and slowly added via syringe. The resulting mixture was stirred in the glove box overnight, leading to formation of a white precipitate. The supernatant was decanted and the residue washed with a small amount of toluene and decanted again. The residue was then redissolved in toluene. After the addition of a small amount of hexanes, a small amount of pink-colored precipitate was observed, which was removed by centrifugation (50 min at 5000 rpm) to give a clear solution. The solution was then precipitated again in hexanes, decanted and dried in vacuum to give the product as a white powder. The residue was redissolved in benzene, filtered through a pipette with a cotton plug, and then freeze dried in vacuum (370 mg, 47 %). Samples for DSC, TGA and elemental analysis where dried for 12 h at 60 °C in vacuum.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.07$  (br, 6H, CH<sub>3</sub>), 1.77-2.55 (br m, 3H, H1/2), 3.58 (br, 4H, CH<sub>2</sub>) 6.53-7.13 (br m, 6H, H4/9/10), 7.37-7.69 (br m, 2 H, H5) ppm. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 1.07$  (br, 6H, H2), 1.43-2.2 (br m, 3H, H1/2), 3.59 (br, 4H, CH<sub>2</sub>) 6.34-7.01 (br m, 6H, H4/9/10), 7.06-7.46 (br m, 2H, H5) ppm. <sup>13</sup>C NMR (125.75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 16.1$  (CH<sub>3</sub>), 37.6 (CH<sub>2</sub>), 40-44 (br, C1/2), 109.2 (C10), 119.3 (C9), 128.5 (br, C7), 131.1 (br, C5), 133.9 (br, C4), 137.2 (C8), 146.0 (br, C3) ppm. <sup>13</sup>C NMR (125.75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 16.3$  (CH<sub>3</sub>), 37.8 (CH<sub>2</sub>), 40-44 (br, C1/2), 108.6 (C10), 118.5 (C9), 127.5 (br, C7), 130.1 (br, C5), 133.4 (br, C4), 137.0 (C8) 145.8 (br, C3) ppm. <sup>11</sup>B NMR (160.411 MHz, CDCl<sub>3</sub>):  $\delta = 25$  ppm ( $w_{1/2} = 1200$  Hz). GPC-RI for product from Method II (THF vs. PS standards):  $M_n = 58000$ ,  $M_w = 81900$ , PDI = 1.41; TGA (20 °C/mir, N<sub>2</sub>): 82% weight loss between 427 °C and 457 °C; 8% residual mass at 800 °C. Elemental analysis for (C<sub>10</sub>H<sub>2</sub>BN<sub>2</sub>): calculated C 78.28, H 7.66, N 10.14%: found C 76.48, H 7.59, N

analysis for  $(C_{18}H_{21}BN_2)_n$ : calculated C 78.28, H 7.66, N 10.14%; found C 76.48, H 7.59, N 9.60%. The slightly low carbon value could be due to trace amounts of ammonium salts or due to incomplete combustion, a phenomenon commonly observed for boron-containing polymer.

**Synthesis of Polymer 3b.** In a glovebox, a solution of poly(4-trimethylsilyl styrene) (1, 300 mg, 1.68 mmol SiMe<sub>3</sub> groups) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added to a solution of BBr<sub>3</sub> (469 mg, 1.87 mmol, 1.1 equiv) in 5 mL CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred for 24 h. A solution of N,N'-diphenyl-1,2-diaminobenzene (1.02 g, 3.92 mmol, 2.3 equiv) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. The mixture was stirred overnight, leading to formation of a white precipitate. The insoluble salts were filtered off by passing the solution through a fritted glass funnel inside the glove box. The polymer was then precipitated by addition of the solution into 80 mL of hexanes. After washing with a small amount of hexanes, the light greyish solid was redissolved in 20 mL of toluene. After filtration, the solution was once again added dropwise to 80 mL of hexanes, the resulting precipitate was collected on a fritted glass funnel and washed with a small amount of hexanes. The product was dried in high vacuum at 50 °C for 12 h to give an off-white powdery solid. Yield: 520 mg (83 %).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.9$ , 1.3 (br m, 3H, H1/2), 5.9, 6.6, 6.9 (br, 18 H, all aromatic protons) ppm. <sup>13</sup>C NMR (125.75 MHz, CDCl<sub>3</sub>):  $\delta = 40-44$  (br, backbone carbons), 110.2, 120.2, 126.4, 127 (br), 128.0, 129.3, 134.6, 138.0, 140.6, 144 (br) ppm. <sup>11</sup>B NMR (160.411 MHz,

CDCl<sub>3</sub>):  $\delta = 26$  ppm ( $w_{1/2} = 1400$  Hz). GPC-RI (THF vs. PS standards):  $M_n = 66500$ ,  $M_w = 83000$ , PDI = 1.25; GPC-LS (THF, in-line assuming 100% mass recovery):  $M_n = 281100$ ,  $M_w = 315600$ , PDI = 1.12, dn/dc = 0.152/ Elemental analysis for ( $C_{26}H_{21}BN_2$ }<sub>n</sub>: calculated C 83.89, H 5.69, N 7.53%; found C 83.31, H 5.50, N 7.34 %.

### **Thermal Properties**



#### Figure S1.

a) Differential Scanning Calorimetry (DSC) plot of polymer **3a**. The polymer showed a glass transition at 154 °C, which is significantly higher than that of polystyrene ( $T_g = 100$  °C), but comparable to previously reported triarylborane-functionalized polystyrene derivatives.<sup>[3]</sup> We can conclude that a more rigid structure results from functionalization with the diazaborolyl heterocycles.

b) Thermogravimetric Analysis (TGA) plot of polymer **3a**. A small amount of weight loss in the region of 100-250 °C for **3a** is attributed to trace amounts of  $[\text{HNEt}_3]\text{Br}$ , which proved to be difficult to remove despite numerous attempts by repeated precipitation, dialysis, and thermal treatment under high vacuum.

**Molecular Weight Determination** 



**Figure S2.** Comparison of GPC traces of the silvlated precursor polymer **1** (top), and the diazaborolyl-functionalized polymers **3a** (middle, R = Et) and **3b** (bottom: R = Ph) (THF, 1.0 mL min<sup>-1</sup>).



**Figure S3.** GPC-PDA plot of polymer **3b** (THF, 1.0 mL min<sup>-1</sup>), which illustrates chromophore incorporation into the polymeric material, indpendendent of the molecular weight.

### **Optical Properties**

Polymer	Solvent	$\lambda_{A,max}$	$\lambda_{exc}$	$\lambda_{E,max}$	ε <sup>[a]</sup>	τ	$\varphi_{\rm F}$
		[nm]	[nm]	[nm]	$[M^{-1} cm^{-1}]$	[ps]	
3a	$CH_2Cl_2$	295	292	360	8290	780	0.77
3b	$CH_2Cl_2$	297	293	360	7840	820	0.51
3b	film	303	269/ 330	364	-	930- 1400	0.10

Table S1: Optical properties of polymers 3a and 3b.

**Photobleaching at Different Excitation Wavelengths.** We also investigated the fading of the fluorescence signal after excitation at different wavelengths. Because energy content and absorption depend on the wavelength of irradiation, the lifetime of the photodegradation process should be related to the excitation wavelength. The differences in the relaxation curves in Figure S4 are consistent with a dependence on the wavelength of irradiation. However, the proximity of the irradiation wavelength to the absorption maximum (*the relative absorbance*) of **3a** has a greater impact on the fading lifetime than the actual energy of the light source.



Figure S4. Photobleaching Studies on 3a: Fading Curves at Different Excitation Wavelengths.

#### **Thin Film Studies**

The absorption and emission spectra of a thin film of polymer **3b** are shown in the main manuscript in Figure 2. The excitation spectrum of polymer **3b** is shown in Figure S5.



Figure S5. a) Excitation spectra of 3a and 3b in CH<sub>2</sub>Cl<sub>2</sub> solution and b) of a thin film of 3b.

The excitation maximum is red-shifted by roughly 30 nm compared with the excitation maximum in  $CH_2Cl_2$  solution. The partial overlap of the excitation and emission bands may contribute to the lower quantum yield in the thin film state, as a result of reabsorption effects.

The lifetime of the thin film was measured in a TCSPC (time-correlated single-photon counting) experiment, because our original time-resolved-LIF setup was not available. Figure S6 shows the decay curves with fitting, instrument response function (IRF) and residuals for polymer **3b**. The detected lifetime of 0.93 - 1.4 ns proved to be at the limit of the effective measuring range for this setup, because of significant overlap from the IRF curve and the experimental data curve, which reflects the fact that the pulse of our light source was already approximately 1 ns long.



Figure S6. Decay curves with fitting, instrument response function (IRF) and residuals for a thin film of polymer 3b.

NMR Spectra





Figure S8. <sup>1</sup>H-NMR spectrum of 3a in  $CD_2Cl_2$ 



Figure S9. H,H-COSY-NMR spectrum of 3a in  $CD_2Cl_2$ 



Figure S10. <sup>13</sup>C-NMR spectrum of 3a in  $CD_2Cl_2$ 



Figure S11. HMQC-NMR spectra of 3a in CD<sub>2</sub>Cl<sub>2</sub>



Figure S12. <sup>11</sup>B-NMR spectrum of 3a in CDCl<sub>3</sub>



Figure S13. <sup>1</sup>H-NMR spectrum of 3b in CDCl<sub>3</sub>



Figure S14. <sup>13</sup>C-NMR spectrum of 3b in CDCl<sub>3</sub>



Figure S15. <sup>11</sup>B-NMR spectrum of 3b in CDCl<sub>3</sub>

## **References**

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