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Preparation of a Polymer-Supported Fluorene-Based Receptor for Quantitative and Efficient Binding of Silver Cations

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Abstract: We have designed and synthesized a polymer-supported material in which a versatile fluorene-*p*-xylene-based receptor is woven onto the backbone of polystyrene. This polymer-supported receptor adopts a π-prismand-like conformation through a simple C–C bond rotation that results in the quantitative binding of a single silver cation per receptor site with a remarkable efficiency that exceeds the binding abilities of the well-known tris[2.2.2]-*p*-cyclophane (or π prismand) by at least a factor of 100. More importantly, the binding event can be readily monitored by ^{1}H NMR spectroscopy, as well as by a more sensitive emission spectroscopic technique in which the quenching of fluorescence of the receptor moiety is quantitatively related to the binding of silver cations.

Keywords: fluorescence spectroscopy · polymer-supported materials · receptors · sensors · silver

Introduction

The design and syntheses of polymeric materials containing multiple functional sites continues to attract considerable attention owing to their potential applications in the areas ranging from catalysis and synthesis to molecular electronics and nanotechnology.[1] The preparation of such polymeric materials is generally carried out either by polymerization of a pre-functionalized monomer or by an attachment of the functional units to a polymeric backbone through a covalent-bond-forming reaction. A number of such materials using functionalized polystyrenes have been synthesized for a variety of applications, such as benzoylated polystyrenes for photochemical polymerization reactions, sulfonated polystyrenes as acid catalysts, polystyrenes functionalized with diphenylphosphino groups for the preparation of palladium and nickel catalysts for C–C bond-forming reactions, and polystyrenes functionalized with diarylamino groups for the preparation of electron-transfer catalysts.[2–5]

We have recently introduced[6] a versatile fluorene-based receptor (**1**), from readily available precursors, that adopts a π-prismand-like[7a] (or analogous doubly bridged deltaphane-like[7c]) conformation through a simple C–C bond rotation. This conformational adaptability of **1** allows it to bind a single silver cation with a remarkable efficiency ($K \approx 15\,000\,\text{M}^{-1}$) that exceeds the binding abilities of the well-known tris[2.2.2]-*p*-cyclophane[7a] (or π-prismand) **2** by at least a factor of 100 (Figure 1).

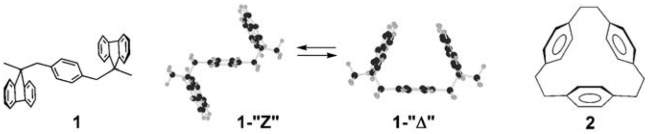

Figure 1. Optimized structures of the (almost) isoenergetic conformers of **1** by density functional theory (DFT) calculations at the B3LYP/6-31G* level and its similarity to the tris[2.2.2]-*p*-cyclophane (or π prismand) (**2**).

We conjectured that weaving such an efficient silver-cation receptor onto the polystyrene (PS) backbone would lead to materials that may possess potentially interesting physical and chemical properties as well as to the development of novel potentiometric and optical silver-ion sensors.[8] Moreover, the highly emissive nature of the fluorene moieties, which constitute the receptor moieties in **3b-PS**, will allow the ready monitoring of the binding events by emission spectroscopy.

Accordingly, herein we report the synthetic route of incorporating receptor unit **3** into the backbone of readily available poly(4-chloromethylstyrene)[9] ($M_w \approx 20\,000$), through a simple nucleophilic substitution reaction (Scheme 1). The binding of the silver cations to the polymer-supported mate-

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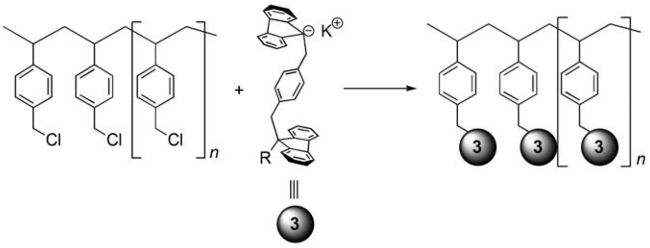


Scheme 1. Incorporation of the silver cation receptor **3** onto a polystyrene backbone.

rial was probed by ^{1}H NMR spectroscopy as well as by a more sensitive emission spectroscopic technique. The details of these findings are discussed below.

Results and Discussion

Synthesis: Initial attempts to incorporate the receptor unit **3a** ($R = CH_3$) into poly(4-chloromethylstyrene) led to the formation of a material that was only sparingly soluble in common organic solvents such as dichloromethane, acetone, and chloroform. The solubility problem was overcome by replacement of the methyl substituent on the 9-position of one of the fluorene moieties with a long alkyl chain (i.e., **3b**, in which R = *n*-hexyl) according to Scheme 2. Thus, a one-pot reaction of fluoranyl anions, generated using *n*-butyllithium at −78 °C, with 1-bromohexane, followed by a further lithiation and reaction with ethyl-4-(bromomethyl)benzoate, afforded **4b** in excellent yield. Reduction of **4b** with lithium aluminum hydride formed the corresponding benzyl alcohol **5b**, which was transformed into the corresponding benzyl chloride **6b** by a reaction with thionyl chloride in chloroform at ≈0 °C in >80 % yield. Reaction of fluoranyl anions, generated from fluorene and *n*-butyllithium at −78 °C, with **6b** finally produced the receptor moiety **3b**. The attachment of receptor **3b** to poly(4-chloromethylstyrene) (**Cl-PS**) was accomplished by its reaction with **3b** in THF in the presence of potassium *tert*-butoxide as a base at ≈0 °C in quantitative yield. The incorporation of receptor **3b** onto the backbone of polystyrene was quantitatively achieved as confirmed by ^{1}H/^{13}C NMR spectroscopy in $CDCl_3$ at 22 °C (Figure 2).

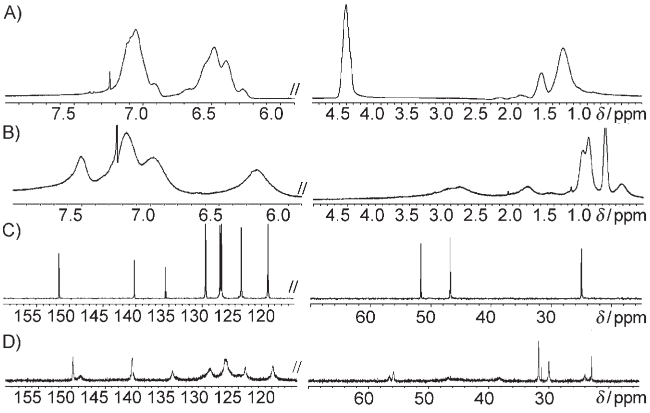
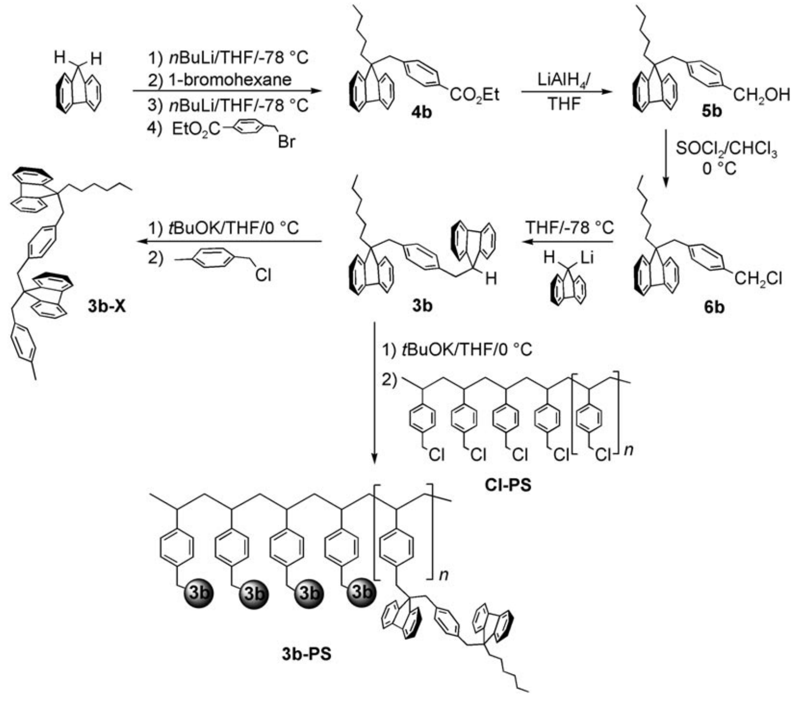


Figure 2. The ^{1}H NMR spectra of A) the starting poly-(4-chloromethylstyrene) (**Cl-PS**) and B) the receptor-linked polystyrene (**3b-PS**), which shows the disappearance of the $-CH_2Cl$ signal at $\delta \approx 4.4$ ppm. The ^{13}C NMR spectra of C) monomeric receptor **1** and D) **3b-PS**, which display the similar chemical shifts of the signals in the aromatic region are also shown.



Scheme 2. Synthesis of the receptor-bound polystyrene **3b-PS** and a model compound **3b-X**.

Model receptor **3b-X** was similarly prepared by reaction of **3b** with α-chloro-*p*-xylene in THF in the presence of potassium *tert*-butoxide as a base (Scheme 2).

Monitoring of Ag$^+$ binding by ^{1}H NMR spectroscopy: The binding of silver cations to the polymeric receptor **3b-PS** was monitored by the changes in the ^{1}H NMR spectrum of **3b-PS** in $CDCl_3$ (0.04 mM per receptor unit) caused by an incremental addition of a concentrated solution of silver trifluoromethanesulfonate (0.4 mM) in a $CDCl_3$/[D$_4$]methanol (1:1) mixture. Notably, the addition of the Ag$^+$ solution to **3b-PS** resulted in significant shifts of the aromatic signals up to the addi-

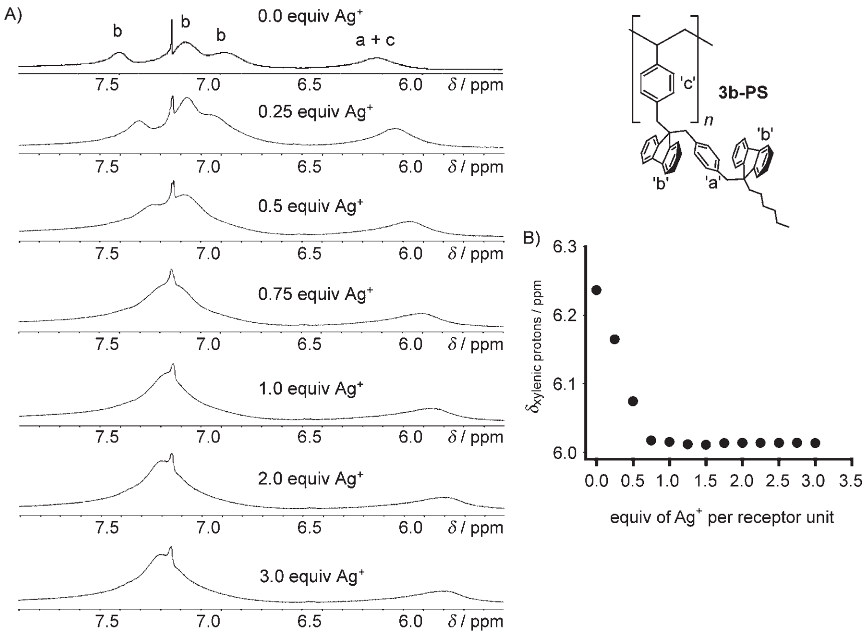


Figure 3. A) Partial ^{1}H NMR spectra of **3b-PS** in $CDCl_3$ (0.04 mm) obtained upon an incremental addition of a 0.4 mm solution of $Ag^+CF_3SO_3^-$ in $CDCl_3$/[D$_4$]methanol (1:1) at 22 °C. B) A plot of changes in the chemical shifts of xylenic protons (from Figure 3A) against the added equivalents of $Ag^+CF_3SO_3^-$ per receptor unit of **3b-PS**.

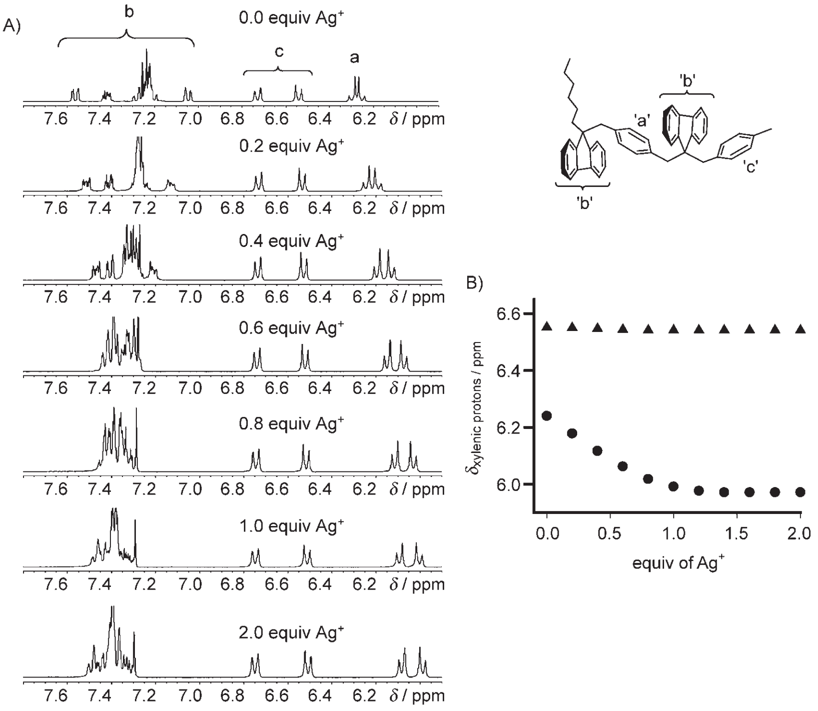


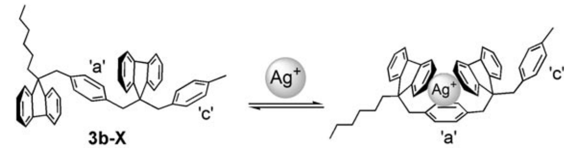
Figure 4. A) Partial ^{1}H NMR spectra of **3b-X** in $CDCl_3$ (0.04 mm) obtained upon an incremental addition of a 0.4 mm solution of $Ag^+CF_3SO_3^-$ in $CDCl_3$/[D$_4$]methanol (1:1) at 22 °C. B) A plot of changes in the chemical shifts (from Figure 4A) of the inner xylenic protons ('a': ●) and outer xylenic protons ('c': ▲) against the equivalents of added Ag$^+$ solution at 22 °C.

tion of one equivalent of Ag$^+$ per receptor unit, as shown in Figure 3A. Moreover, the ^{1}H NMR spectrum remained unchanged upon further addition of the Ag$^+$ solution (i.e., beyond 1 equiv per receptor unit), as shown in Figure 3B.

It is noteworthy, based on our previous studies,[6] that if the silver cation binds in the Δ-shaped cavity, formed by the two fluoranyl rings (labeled 'b') and one inner xylene moiety (labeled 'a'), the chemical shift of the outer xylenic protons (labeled 'c') should be largely unaffected. Unfortunately, the ^{1}H NMR spectra displayed in Figure 3A did not show a clear distinction between the two sets of xylenic protons (labeled as 'a' and 'c') due to the extensive overlapping and broadening of the signals. Therefore, we employed model compound **3b-X** to probe the Ag$^+$ binding event in **3b-PS** as follows.

A similar ^{1}H NMR spectral titration of **3b-X** in $CDCl_3$ (0.04 mm) by an incremental addition of a solution of Ag$^+$ (0.4 mm) in $CDCl_3$/[D$_4$]methanol (1:1) showed significant chemical shift changes (up to the addition of 1 equiv of Ag$^+$ solution) in the ^{1}H NMR signals arising from two fluoranyl rings and one inner xylene ring (see Figure 4A). As expected, the signals arising from the outer xylenic ring (labeled as 'c') remained unchanged (see Figure 4A and B). Such an observation confirms that the Δ-shaped cavity is comprised of two fluoranyl and one interconnecting xylene ring in the receptor **3b-X**, whereas the outer xylene ring (labeled as 'c') does not participate in the Ag$^+$ complexation (Scheme 3).

As shown in Figure 3, the ^{1}H NMR spectral changes for **3b-PS** upon complexation with silver cations were rather similar to those observed for the model receptor **3b-X** (see Figure 4). In both polymeric receptor **3b-PS** and model receptor **3b-X**, the fluorene protons merge together at $\delta \approx 7.2$–7.3 ppm while the inner xylenic protons shift up-field (by $\delta \approx 0.25$ ppm); such a similarity in the spectral changes



Scheme 3. The encapsulation of Ag$^+$ inside the Δ-shaped cavity, which is formed by the two fluoranyl rings and one inner xylene moiety.

lends support to the fact that the polymer-supported receptor moieties undergo a similar conformational change to the model receptor **3b-X** upon complexation with silver cations (Scheme 3).

Monitoring of Ag$^+$ binding by emission spectroscopy: Firstly, the characteristic emission and excitation spectra of solutions of various receptors, **1**, **3b-X**, and **3b-PS**, in dichloromethane at 22 °C are shown in Figure 5. It is noteworthy that the excitation/emission spectra of **1**, **3b-X**, and **3b-PS** were characteristically similar to those observed for the parent fluorene,[10] therefore suggesting that the emission characteristics of the fluorene moieties are not altered by their incorporation into the polystyrene framework.

As shown in Figure 6, the emission arising from the solutions of **1**, **3b-X**, and **3b-PS** in dichloromethane was instantaneously quenched upon exposure to a solution of Ag$^+$ CF$_3$SO$_3^-$ in methanol at 22 °C. For example, $>90\,\%$ of the emission (at $\lambda = 318$ nm) of **1** (or **3b-X** or **3b-PS**) was quenched by the incremental addition of one equivalent of a solution of silver trifluoromethanesulfonate in methanol (1.0×10^{-4} M) to a solution of **1** (or **3b-X** or **3b-PS**) in dichloromethane (6.36×10^{-6} M per receptor unit).

Interestingly, roughly $\approx 10\,\%$ emission of the fluorene moieties in various receptors was only quenched when an excess of Ag$^+$ solution (i.e., ≈ 1.5 equiv) was added. This observation is in contrast to our ^{1}H NMR spectroscopic titrations (Figures 3 and 4), which showed that there was no change in the ^{1}H NMR spectra beyond the addition of one equivalent of silver cations. Moreover, unlike the ^{1}H NMR spectroscopic titrations with silver cations, the changes in emission intensities were not proportional to the number of equivalents of added Ag$^+$ solution (compare Figures 3, 4, and 6). Such an observation is tentatively reconciled by the fact that the timescales for NMR and emission measurements, as well as the sensitivity of these two techniques are vastly different. It is conceivable that the dynamic nature of the Ag$^+$ binding to **1**, **3b-X**, **3b-PS** may result in a certain percentage of the host fluorene moieties being distant from

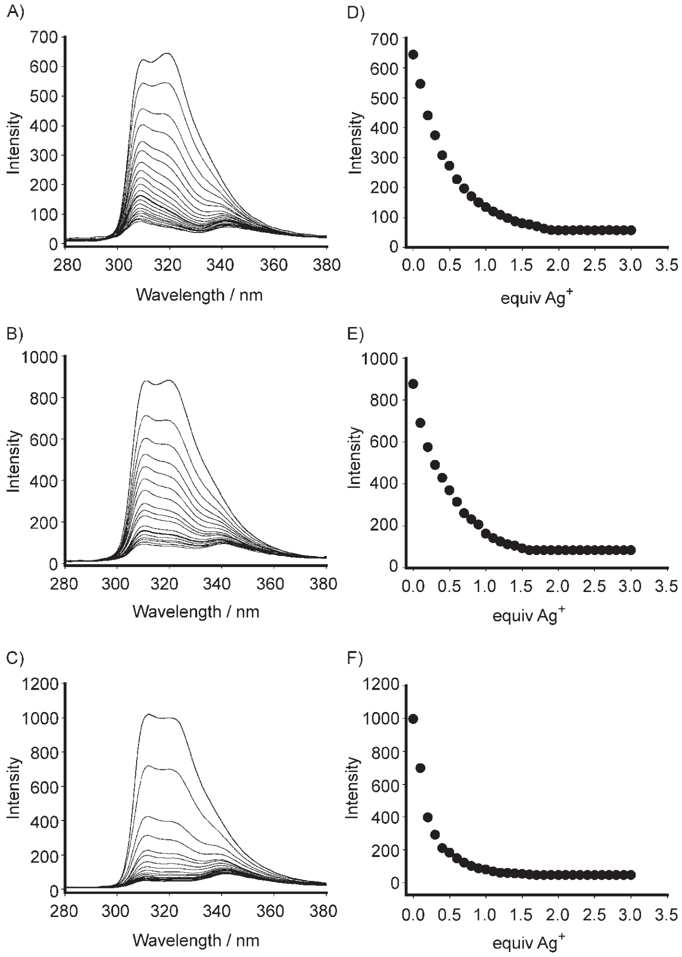


Figure 6. Left: Emission spectra of receptors A) **1**, B) **3b-X**, and C) **3b-PS** in dichloromethane (6.36×10^{-6} M) upon an incremental addition of a 1×10^{-4} M solution of Ag$^+$CF$_3$SO$_3^-$ in methanol at 22 °C. Right: Plots of changes in the emission intensity of D) **1**, E) **3b-X**, and F) **3b-PS** at 318 nm against the added equivalents of a solution of Ag$^+$CF$_3$SO$_3^-$ per receptor unit at 22 °C.

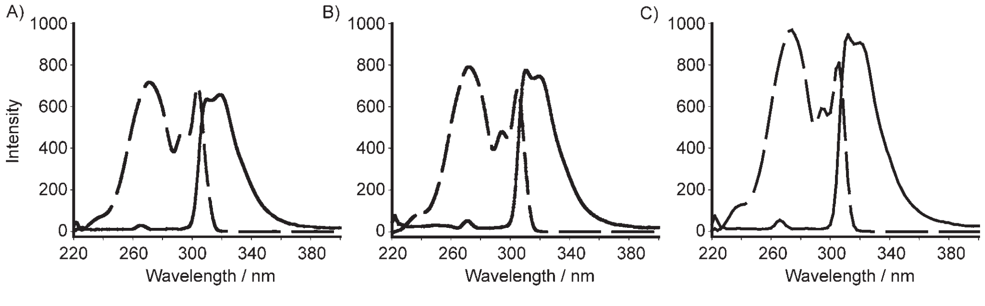


Figure 5. Emission (——) and excitation (– – –) spectra of a 6.36×10^{-6} M solution of receptors A) **1**, B) **3b-X**, and C) **3b-PS** in dichloromethane at 22 °C obtained by excitation at 270 nm.

the guest silver cations during the emission measurements. None the less, only a modest excess of Ag^+ (i.e., 1.5 equiv) was necessary to fully quench the entire emission of the fluorophores in various receptors (i.e., **1**, **3b-X**, and **3b-PS**).

Conclusion

In summary, we have designed and synthesized a conformationally adaptable silver receptor from readily available starting materials and have shown that it can be easily woven onto the backbone of polystyrene. The polymer-supported receptor **3b-PS** binds quantitatively one equivalent of Ag^+ per receptor unit, as monitored by ^1H NMR spectroscopy. Also, the Ag^+ binding can be monitored by emission spectroscopy. Moreover, a comparison of the ^1H NMR spectral changes in **3b-PS** to monomeric **1** and **3b-X** suggests that the receptor moieties undergo similar conformational changes into Δ-shaped cavities for efficient capture of silver cations. We are presently exploring the solid-state properties of these polymer-supported receptors for potential materials applications as well as their usage in organic synthesis.[11]

Experimental Section

General: Fluorene, 1-bromohexane, *n*-butyllithium, silver trifluoromethanesulfonate, ethyl-4-(bromomethyl)benzoate, α-chloro-*p*-xylene, potassium *tert*-butoxide, thionyl chloride, lithium aluminum hydride, chloroform, hexanes, tetrahydrofuran, and ethyl acetate were commercially available from Aldrich and were used as received unless otherwise specified.

Anhydrous tetrahydrofuran (THF) was prepared by refluxing the commercial THF over lithium tetrahydroaluminate under an argon atmosphere for 24 h followed by distillation. The dry THF was then stored under an argon atmosphere in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. Dichloromethane was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (≈10 % by volume) until the acid layer remained colorless. After separation, the solution was washed successively with water, aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride, and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from P_2O_5 under an argon atmosphere and then heated at reflux over calcium hydride (≈12 h). After distillation from CaH_2, the solvents were stored in Schlenk flasks under an argon atmosphere.

Preparation of 4b: Under an argon atmosphere, *n*BuLi (2.5 M in hexanes, 12 mL) was added dropwise to a cooled (−78 °C) solution of fluorene (5.0 g, 30 mmol) in anhydrous THF (100 mL). After 10 min of stirring, 1-bromohexane (4.2 mL, 30 mmol) was added and the mixture was stirred for an additional 15 min before it was left to warm to room temperature. [Note that it is critical to maintain the temperature at −78 °C throughout the addition of 1-bromohexane and for an additional 15 min to avoid the formation of 9,9-dihexylfluorene.] The resulting reaction solution was recooled to −78 °C, and *n*BuLi (2.5 M in hexanes, 12 mL) was added dropwise to afford a dark-orange mixture, which was stirred for an additional 10 min. Solid ethyl-4-(bromomethyl)benzoate (7.29 g, 30 mmol) was added to this mixture and the cooling bath was removed. The resulting mixture was stirred for 1 h and the reaction was quenched by pouring it onto water (200 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to afford a brown-colored syrup. The crude material was purified by flash chromatography on silica gel using hexanes as an eluent to afford **4b** as a clear oil (10.2 g, 83 %). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.55$ (m, 2H), 0.75 (t, 3H), 1.07 (m, 6H), 1.28 (t, 3H), 2.12 (m, 2H), 3.22 (s, 2H), 4.26 (q, 2H), 6.64 (d, 2H), 7.29 (m, 8H), 7.51 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.50$, 23.06, 26.03, 30.07, 32.06, 33.49, 46.98, 47.85, 51.75, 61.03, 120.13, 123.64, 127.04, 127.36, 128.22, 128.56, 130.19, 140.06, 143.06, 150.62, 166.80 ppm.

Preparation of 5b: Lithium aluminum hydride (1.3 g, 35 mmol) was added carefully to a solution of ester **4b** (9.0 g, 26.0 mmol) in THF (75 mL). The resulting suspension was heated at reflux for 2 h and cooled to room temperature. H_2O (1.4 mL), 15 % aqueous sodium hydroxide (1.4 mL), and H_2O (4.2 mL) were added successively and slowly to this mixture to afford a white slurry, which upon stirring, separated the inorganic component into a solid mass. The organic layer was separated by a simple filtration and the solid mass was triturated with dichloromethane (3 × 100 mL). The combined organic layers were dried over anhydrous magnesium sulfate and filtered. Evaporation of the solvent under reduced pressure afforded **5b** as a colorless oil (8.0 g, 90 %), which was used in the next step without further purification. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.58$ (m, 2H), 0.75 (t, 3H), 1.05 (m, 6H), 2.11 (m, 2H), 3.14 (s, 2H), 4.45 (d, 2H), 6.64 (d, 2H), 6.93 (d, 2H), 7.29 (m, 6H), 7.54 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.27$, 22.83, 23.96, 29.95, 31.71, 39.26, 46.60, 56.08, 65.32, 119.94, 123.90, 126.06, 126.89, 127.12, 130.67, 137.06, 138.49, 141.16, 149.59 ppm.

Preparation of 6b: With the aid of a dropping funnel, a solution of thionyl chloride (1.9 mL, 26 mmol) in chloroform (50 mL) was slowly added to a cold (≈0 °C) solution of alcohol **5b** (8.0 g, 21.6 mmol) in chloroform (100 mL). The resulting mixture was stirred for an additional 30 min at 0 °C and at room temperature for 10 h. The reaction was quenched by a slow addition of 5 % aqueous $NaHCO_3$ (150 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to afford **6b** as a white solid (6.1 g, 73 %), which was sufficiently pure and was used in the next step without further purification. M.p. 64–66 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.58$ (m, 2H), 0.75 (t, 3H), 1.06 (m, 6H), 2.11 (m, 2H), 3.14 (s, 2H), 4.37 (s, 2H), 6.62 (d, 2H), 6.94 (d, 2H), 7.27 (m, 6H), 7.53 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.34$, 22.89, 24.03, 30.00, 31.79, 39.27, 46.50, 46.69, 56.09, 120.04, 123.90, 126.99, 127.24, 127.63, 130.85, 135.11, 138.02, 141.20, 149.50 ppm.

Preparation of 3b: *n*BuLi (2.5 M in hexanes, 6.3 mL) was added dropwise to a pre-chilled (−78 °C) solution of fluorene (2.6 g, 15.7 mmol) in anhydrous THF (75 mL). After 10 min of stirring, solid **6b** (6.1 g, 15.7 mmol) was added and the mixture was stirred for 15 min at −78 °C. The cooling bath was removed and the reaction mixture was stirred for an additional 1 h. The resulting mixture was poured onto water (200 mL) and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined dichloromethane extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to afford a colorless solid. The crude material was purified by flash chromatography on silica gel using hexanes as an eluent to afford **3b** as a white solid (6.0 g, 73 %). M.p. 54–56 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.58$ (m, 2H), 0.74 (t, 3H), 1.07 (m, 6H), 2.14 (m, 2H), 2.84 (d, 2H), 3.18 (s, 2H), 4.00 (t, 1H), 6.50 (d, 2H), 6.76 (d, 2H), 6.86 (d, 2H), 7.27 (m, 10H), 7.57 (m, 2H), 7.69 ppm (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.34$, 22.91, 24.13, 30.04, 31.79, 39.34, 40.04, 46.85, 49.04, 56.40, 119.84, 119.97, 123.97, 125.37, 126.83, 126.95, 127.15, 127.25, 128.35, 130.26, 135.55, 137.43, 140.99, 141.43, 147.15, 149.71 ppm.

Preparation of 3b-X: Under an argon atmosphere, potassium *tert*-butoxide (0.9 g, 8.0 mmol) was added to a cold (≈0 °C) solution of **3b** (1.1 g, 2.0 mmol) in anhydrous THF (40 mL). After 10 min of stirring, α-chloro-*p*-xylene (0.3 g, 2.0 mmol) was added and the mixture was stirred for 15 min at 0 °C. The cooling bath was removed and the reaction mixture was stirred for an additional 8 h at room temperature. The resulting mixture was poured onto water (50 mL) and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined dichloromethane extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to afford a pale-yellow solid. The crude material was purified by recrystallization from dichloromethane/methanol to afford **3b-X** as a white crystalline powder (1.0 g, 80%). M.p. 144–146°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.52$ (m, 2H), 0.78 (t, 3H), 1.00–1.20 (m, 6H), 1.95 (m, 2H), 2.11 (s, 3H), 2.88 (s, 2H), 3.13 (s, 2H), 3.20 (s, 2H), 6.27 (q, 4H), 6.54 (d, 2H), 6.73 (d, 2H), 7.05 (d, 2H), 7.17–7.30 (m, 10H), 7.40 (m, 2H), 7.56 ppm (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.29$, 21.21, 22.87, 23.97, 29.97, 31.68, 38.25, 44.36, 45.71, 46.78, 55.92, 56.81, 119.71, 119.73, 124.00, 124.98, 126.35, 126.74, 126.96, 127.05, 128.07, 129.20, 129.29, 130.30, 134.38, 134.78, 135.02, 135.38, 141.01, 141.03, 148.70, 149.81 ppm.

Preparation of 3b-PS: Under an argon atmosphere, potassium *tert*-butoxide (0.8 g, 7.0 mmol) was added to a solution of **3b** (1.1 g, 2.0 mmol) in anhydrous THF (40 mL) cooled to 0°C. After 10 min of stirring, solid poly(4-chloromethylstyrene) (0.23 g, 1.5 mmol) was added and the mixture was stirred for 15 min at 0°C. The cooling bath was removed and the reaction mixture was stirred for an additional 12 h at room temperature and then heated to reflux for 12 h. The resulting solution was poured onto water (100 mL) and the aqueous layer was extracted with dichloromethane (3×100 mL). The combined dichloromethane extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to afford a yellow solid. The crude material was purified by flash chromatography on silica gel using 50% ethyl acetate/hexanes as an eluent to afford **3b-PS** as a white foam (0.8 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.52$ (m, 2H), 0.77 (m, 3H), 1.02 (m, 8H), 1.58 (m, 1H), 1.90 (m, 2H), 2.92 (m, 6H), 6.24 (m, 6H), 7.12 (m, 12H), 7.52 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.24$, 22.86, 23.91, 30.01, 31.76, 38.28, 46.62, 55.86, 56.87, 119.74, 123.89, 126.93, 129.17, 134.91, 140.29, 148.70, 149.82 ppm.

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[1] a) J. M. Longmire, B. Wang, X. Zhang, *J. Am. Chem. Soc.* **2002**, *124*, 13400–13401; b) C. Wei, Z. Li, C.-J. Li, *Org. Lett.* **2003**, *5*, 4473–4475; c) S. D. Nayak, V. Mahadevan, M. Srinivasan, *J. Catal.* **1985**, *92*, 327–339; d) C. A. McNamara, M. J. Dixon, M. Bradley, *Chem. Rev.* **2002**, *102*, 3275–3300, and references therein.

[2] D. E. Bergbreiter, *Chem. Rev.* **2002**, *102*, 3345–3384, and references therein.

[3] T. J. Dickerson, N. N. Reed, K. D. Janda, *Chem. Rev.* **2002**, *102*, 3325–3344, and references therein.

[4] C. Bianchini, M. Frediani, F. Vizza, *Chem. Commun.* **2001**, 479–480.

[5] N. L. Bauld, D. J. Bellville, S. A. Gardner, Y. Migron, G. Cogswell, *Tetrahedron Lett.* **1982**, *23*, 825–828.

[6] R. Rathore, V. J. Chebny, S. H. Abdelwahed, *J. Am. Chem. Soc.* **2005**, *127*, 8012–8013.

[7] a) J. L. Pierre, P. Baret, P. Chautemps, M. Armand, *J. Am. Chem. Soc.* **1981**, *103*, 2986–2988; b) G. Pierre, P. Baret, P. Chautemps, J. L. Pierre, *Electrochim. Acta* **1983**, *28*, 1269–1271; c) H. C. Kang, A. W. Hanson, B. Eaton, V. Boekelheide, *J. Am. Chem. Soc.* **1985**, *107*, 1979–1985.

[8] Z. Szigeti, A. Malon, T. Vigassy, V. Csokai, A. Gruen, K. Wygladacz, N. Ye, C. Xu, V. J. Chebny, I. Bitter, R. Rathore, E. Bakker, E. Pretsch, *Anal. Chim. Acta* **2006**, *572*, 1–10.

[9] Poly(4-chloromethylstyrene) is commercially available and can also be easily prepared by radical polymerization of 4-chloromethylstyrene, see: D. E. Bergbreiter, C. Li, *Org. Lett.* **2003**, *5*, 2445–2447, and references therein.

[10] D. L. Horrocks, W. G. Brown, *Chem. Phys. Lett.* **1970**, *5*, 117–119.

[11] A. Mandoli, S. Orlandi, D. Pini, P. Salvadori, *Tetrahedron: Asymmetry* **2004**, *15*, 3233–3244.

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