

Novel chemical cyclization routes to prepare ladder-type conjugated molecules

Inja Kim, Minji Yoo and Tae-Hyun Kim*

Department of Chemistry, University of Incheon, Dowha-dong 177, Nam-gu, Incheon 402-749, Republic of Korea

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Abstract—Novel chemical cyclization methods using BBr_3 and fluoride have been successfully developed to produce ladder-type conjugated molecules. Both electron rich and electron poor conjugated polymers were readily prepared by BBr_3 -promoted cyclization method both in solution and on film. Extension of the π -conjugated systems caused by their rigid planar structures was confirmed by the absorption or emission spectroscopy. A fluoride-induced aromatic cyclization method was also developed and an application to fluoride ion sensing scheme was suggested.

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1. Introduction

The photophysical and electrical properties of π -conjugated materials highly depend on the nature of their building units. While new materials are being introduced,¹ ladder-type with planar π -conjugated molecular architectures² are current topics in a broad spectrum of research fields including light-emitting diodes,³ thin film transistors,^{1b,4} molecular-scale devices,⁵ and sensory materials.⁶ The virtue of this class of molecules is their rigid coplanar structures that promise enhanced π -conjugation by their annelated coplanar structure, leading to a set of desirable properties such as high charge carrier mobility and chemical/thermal stability.

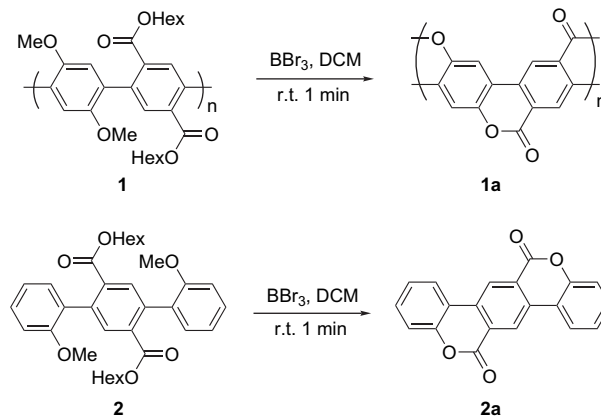
These rigid systems are, however, very difficult to prepare and generally insoluble because of their strong π -stacking interactions, which limit their purification to vacuum sublimation methods. Owing to the major impact of impurity on the performance of organic electronic devices, the definition of synthetic methods allowing simple and straightforward purification of organic semiconductors appears as a key issue for the development of new materials. Several groups have reported the preparation of soluble, thermally or photochemically sensitive, precursors allowing the direct formation of active films of ladder-type compounds.⁷ Nevertheless, the synthetic routes are limited mainly to pentacene derivatives, and hence are not very versatile.

In a previous communication, we have demonstrated the BBr_3 -promoted cyclization method to produce ladder-type

conjugated systems.⁸ To the best of our knowledge, no practical approach for the preparation of these rigid systems has been reported before. Herein, we present in detail the development of this methodology and further extensions.

2. Results and discussion

The ladder-type conjugated polymer **1a** was prepared from polymer **1** by the addition of BBr_3 in dichloromethane (Scheme 1).⁸ Phenoxide, generated by BBr_3 -promoted demethylation, acted as a nucleophile for acyl substitution with the neighboring ester group, causing to instantaneously lactonize to **1a** in a quantitative yield. The cyclized polymer **1a** was insoluble in most organic solvents attempted, and was stable against air and moisture because of its rigid structure.



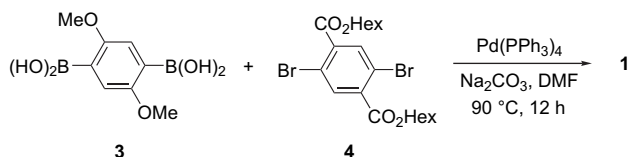
Scheme 1. Preparation of the ladder-type ester polymer **1a** and its corresponding model compound **2a** by BBr_3 -promoted lactonization.

Keywords: Chemical cyclization; Conjugated molecule; Ladder-type structure; Fluoride sensor.

* Corresponding author. Tel.: +82 32 770 8232; fax: +82 32 770 8238; e-mail: tkim@incheon.ac.kr

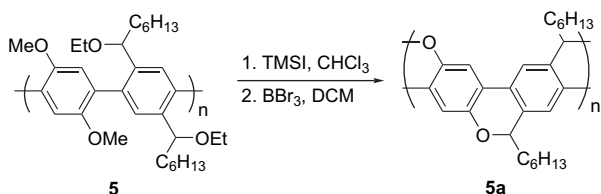
The structure determination of polymer **1a** was carried out by the comparative spectroscopic method with the model compound **2a**. The IR spectrum of **1a** showed a predominant carbonyl signal corresponding to a lactone at 1731 cm^{-1} , compared with that of an ester (1720 cm^{-1}) for **1**, and this was consistent with the results from the model compounds **2** and **2a** (1721 cm^{-1} for **2** and 1732 cm^{-1} for **2a**).⁹

Synthesis of the precursor **1** for the ladder-type polymer **1a** was achieved by employing the Pd-catalyzed cross-coupling protocol using the corresponding diboronic acid **3** and dibromoester **4** (Scheme 2).



Scheme 2. Synthesis of the precursor polymer **1** using Pd-catalyzed Suzuki cross-coupling reaction.

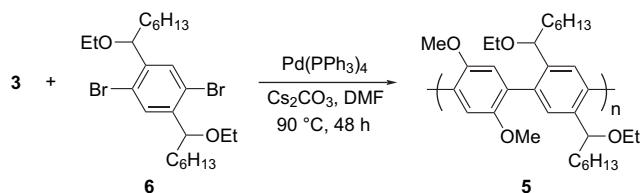
Our chemical cyclization method using BBr_3 has expanded its utility to produce the ether-type ladder polymer **5a** (Scheme 3). BBr_3 -promoted demethylation caused nucleophilic substitution of the phenoxide with the benzyl iodide, which was prepared by reacting the ethoxy polymer **5** with TMSI,¹⁰ to afford the cyclized benzyl ether **5a**.¹¹



Scheme 3. Preparation of the ladder-type ether polymer **5a** using BBr_3 .

In addition to the rigid structure, brought by its planar platform, polymer **5a** holds further advantage of solubility in organic solvents due to the presence of long alkyl chains. Indeed, polymer **5a** is readily soluble in THF and dichloromethane, and any by-products formed during the cyclization can thus be easily removed by a Soxhlet method.

The polymer **5** was obtained by the Pd-catalyzed cross-coupling reaction of the diboronic acid **3** with the corresponding dibromide **6** (Scheme 4).



Scheme 4. Synthesis of the precursor polymer **5** using Pd-catalyzed cross-coupling reaction.

The electronic properties of the cyclized polymer (**5a**) were studied by the fluorescence spectroscopies both in solution and on film, and compared to the corresponding noncyclized

precursor **5**. As expected, the emission spectra of the cyclized polymer **5a** showed a significant red-shift compared to its precursor **5**, and this was more evident on the solid state (Fig. 1 and Table 1). This result clearly indicated that the BBr_3 -promoted intramolecular cyclization transformed a flexible nonplanar weakly conjugated chromophore into a highly delocalized system with rigid ladder-type planar structure.

In addition to the bathochromic spectral change, the transformation from a flexible chromophore to a rigid extended one further caused a dramatic increase in the emission efficiency of **5a** in solution by reducing the nonradiative rate ($\Phi=21\%$ for **5** and 50% for **5a**; Table 1). The geometrical (vibrational–rotational) changes in the excited state of **5**, which facilitate nonradiative processes were reduced by inhibiting rotation about the phenyl–phenyl bond, rendering a strong fluorescence in **5a**.

Cyclization of the polymer **1** was successfully achieved not only in solution but also on films. Any residues of the cyclization reaction were believed to be removed by washing the film and only insoluble cyclized polymer **1a** remained afterward. Figure 2 shows the UV–vis absorption spectra of compounds **1** and **1a** on films.^{8,12} The spectrum of compound **1** shows an absorption maximum at 366 nm. In contrast, compound **1a** shows a maximum at 390 nm, which confirms that the planarization of the structure due to the cyclization makes an effective extended conjugation.

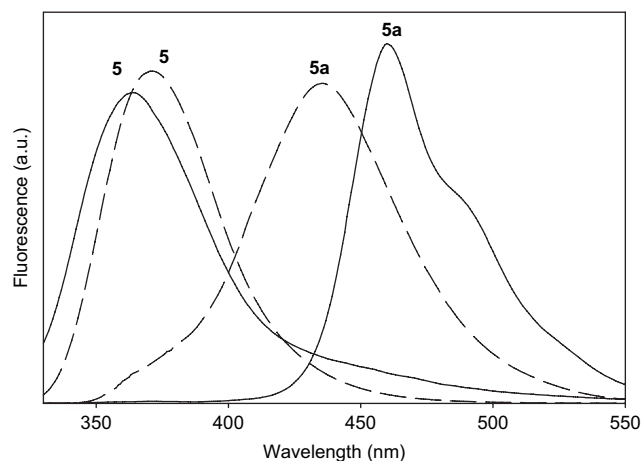


Figure 1. Emission spectra of the precursor polymer **5** and its cyclized form **5a** in dichloromethane solution (dotted line) and on film (solid line).

Table 1. Photophysical data in dichloromethane

Compound	Abs. max. ^a (log ϵ)	Emission max. ^a	Φ [%] ^b
5	309 (4.06) ^c	366	21
5^d	310	371	—
7	255 (5.66)	—	<0.01
5a	376 (4.06) ^c	441	52 ^e
5a^d	383	455	—
7a	256 (6.68)	336	46

^a Given in nanometers.

^b Determined with 2-aminopyridine as a standard.

^c Per monomer unit.

^d Data on film.

^e Determined with quinine sulfate as a standard.

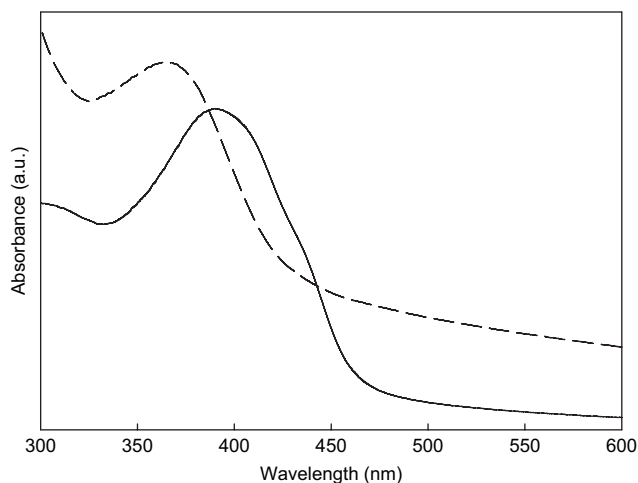
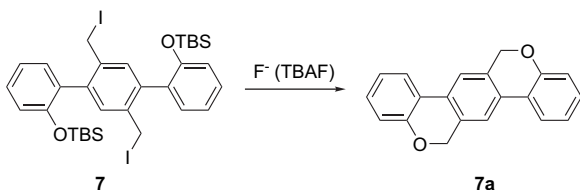


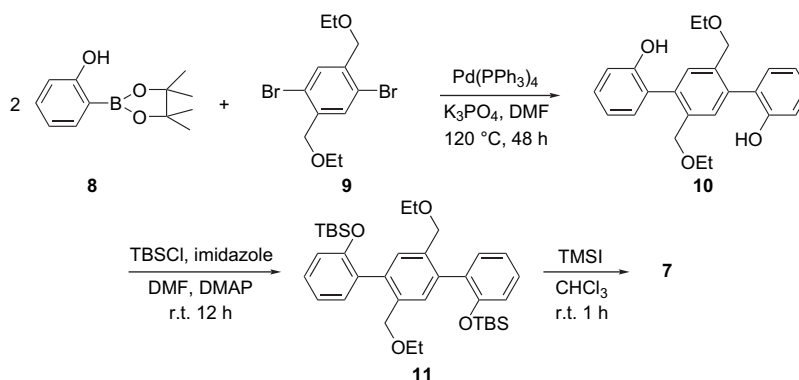
Figure 2. UV-vis spectra of precursor polymer **1** (dotted line) and its cyclized form **1a** (solid line) on films. The spectrum of **1a** was obtained after dipping the film of **1** into a solution of BBr_3 (1.0 M in hexane) and a little amount of dichloromethane for 1 min, followed by washing with methanol and water.



Scheme 5. Fluoride-induced cyclization of the indicator **7** led to the fluorescent molecule **7a** with a planar structure.

The possibility to prepare thin-films of the ladder-type conjugated polymers, associated with their planar conformation, incites us to realize field-effect transistors using these novel rigid polymers (**1a** and **5a**) as active semiconductor layers. The cyclized ether polymer **5a**, having an electron-donor, was regarded as a suitable candidate for a p-type polymer, whereas the cyclized ester polymer with an electron-acceptor **1a** would be an n-type counterpart. We expect that these novel cyclized conjugated polymers with rigid planar structure would provide high mobility, together with significant environmental stability.¹³ Possibilities of the prepared films for organic field-effect transistors are currently under investigation.

Finally, to further exploit our chemical cyclization route, we have also developed a fluoride-induced cyclization scheme,



Scheme 6. Synthetic route to the sensory molecule **7**.

where the fluoride-induced cyclization caused planarization of the aromatic units. The phenoxide, generated from the fluoride-induced desilylation in **7**, reacted with the neighboring benzyl iodide, leading to form a fluorescent molecule **7a** (Scheme 5).

This method constitutes a significant advantage over the BBr_3 -promoted cyclization as it can be used as a fluoride ion sensing scheme.^{14,15} In fact, the originally nonfluorescent compound **7** displayed strong fluorescence upon fluoride-induced cyclization (Fig. 3). The indicator **7** was highly selective to fluoride ion and was, indeed, stable to an excess of chloride or iodide ion.

Monitoring the reaction in situ by measuring the fluorescence intensity revealed that the rate of cyclization reactions (**7** to **7a**) was found to be first order in **7** with the rate constant (k) of $2 \times 10^{-2} \text{ s}^{-1}$, and independent of fluoride. This result indicates that the silyl cleavage (or fluoride association with the silyl group) is fast and that cyclization is the slow step. The cyclization of **7** to **7a** effected by fluoride ion (in the form of its tetrabutylammonium salt) in THF solution reached a complete conversion in just 2 min with only two equimolar of fluoride ion relative to the indicator **7** (Fig. 3).

Synthesis of the sensory molecule **7** is shown in Scheme 6. The diethoxy terphenyl **10** was obtained by the Pd-catalyzed

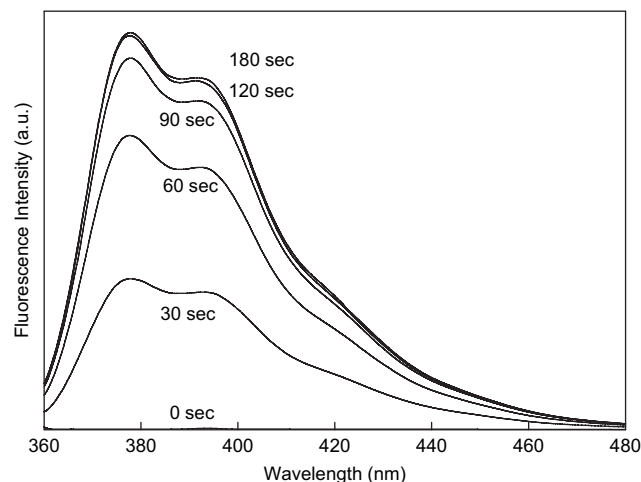


Figure 3. Emission spectral changes upon addition of TBAF to **7** in THF: **7**, $3.5 \times 10^{-6} \text{ M}$ and TBAF, $7 \times 10^{-6} \text{ M}$.

cross-coupling reaction of the corresponding borate **8** with the dibromide **9**. Silylation of the phenol in **10** using TBDMSCl afforded **11**.¹⁶ Finally, the ethoxy benzyl group in **10** was transformed into the corresponding iodo benzyl group as in **7** using TMSI.¹⁰

3. Conclusion

We have demonstrated the chemical cyclization method to produce novel ladder-type conjugated systems by the use of BBr₃. Both electron rich and electron poor conjugated polymers were successfully prepared by this method. The prepared conjugated polymer with alkyl chains belongs to a few examples of the soluble ladder-type structure. The rigid planar structure caused an extension of the π -conjugated systems, together with environmental stability.

A fluoride-induced aromatic cyclization method was also developed and this was applied to fluoride ion sensing system. Although this system is inevitably irreversible, our sensory approach is highly selective for fluoride ion as it is based on the specific affinity of fluoride to silicone.

4. Experimental

4.1. General methods

Melting points were determined using Büchi 510 melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet MAGNA 560-FTIR spectrometer. ¹H NMR spectra were recorded on a Bruker Advance DPX-300 and DPX-500 instruments using deuteriochloroform as reference or internal deuterium lock. The chemical shift data for each signal are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS)=0, and referenced to the residual solvent. ¹³C NMR spectra were recorded on a Bruker Advance-500 (125.7 MHz) instrument using internal deuterium lock and proton decoupling. Mass spectra were obtained on a JEOL JMS-AX505WA instrument. UV–vis absorption spectra and fluorescence spectra were measured with Hewlett Packard 8452A diode array spectrometer and SPEX Fluorolog- τ 2 fluorometer (model FL 112, 450 W, xenon lamp), respectively, using spectral grade THF or CH₂Cl₂ as a solvent. The measurements were carried out at 25 °C using a quartz cell with a path length of 1 cm. The kinetic studies for the cyclization of the indicators **7** in dichloromethane were followed by measuring the fluorescence spectra after mixing **7** with TBAF in a quartz cell. The reaction was carried out at room temperature under the excess amount of TBAF (initial concentration [indicator] \ll [TBAF]) and the reaction was expected to reach 100% conversion of **7** to **7a**. Separate solutions of different concentrations of **7** with TBAF in THF were prepared and mixed to investigate the kinetics. In all cases, the concentration was low enough to maintain a UV absorption that was below 0.1. The rate of the cyclization was determined by fitting the fluorescence intensities of the samples to the pseudo-first order equation:

$$\ln \frac{F_{\max} - F_t}{F_{\max}} = -kt, \quad (1)$$

where F_t and F_{\max} are the fluorescence intensities at the monitoring wavelengths at time t and the maxima values, which are the last fluorescence intensities when the cyclization of the indicator **7** reached the conversion of 100%. k is the apparent rate constant. Molar masses were determined by gel permeation chromatography (GPC) using two PL Gel 30 cm 5 μ m mixed C columns at 30 °C running in THF and calibrated against polystyrene ($M_n=600 \times 10^6$ g/mol) standards using a Knauer refractive index detector.

Reagents were purified and dried by standard technique. All air and water-sensitive synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques.

4.1.1. General methods.¹⁷

4.1.1.1. Synthesis of the polymer 5. A solution of the dibromoester **6** (0.50 g, 0.96 mmol) in freshly distilled DMF (7 mL) was degassed by bubbling nitrogen through the solution for 30 min. Pd(PPh₃)₄ (75 mg, 0.048 mmol), diboronic acid **3** (0.38 g, 0.96 mmol), triphenylphosphine (0.05 g, 0.19 mmol), and Cs₂CO₃ (1.25 g, 3.84 mmol) were added sequentially to the solution. The mixture was stirred at 90 °C for 48 h to yield a pale yellow suspension. The mixture was cooled to room temperature and water (2 mL) was added. A pale yellow solid was collected by suction filtration. The filtrate was dissolved in CHCl₃ then precipitated into methanol followed by stirring. This was repeated twice and the polymer **5** was obtained as a pale yellow solid (0.3 g, 60%); ¹H NMR (300 MHz, CDCl₃, δ) 7.2–7.1 (2H, br signal), 6.8–6.7 (2H, br signal), 4.2 (2H, br signal, 2 \times ArCH), 3.60 (6H, br singlet, 2 \times OCH₃), 3.5–3.2 (4H, br signal), 1.5–1.3 (6H, br signal), 1.2–1.1 (20H, br signal), and 0.78 (6H, br signal); GPC (THF, RI) Da M_n 6.8 \times 10³, M_w 8.7 \times 10³ and M_w/M_n 1.3; ν_{\max} (KBr)/cm⁻¹ 3048, 2930, 2851, 1463, 1397, 1211, and 1092.

4.1.1.2. Cyclization of polymer 5 to produce 5a. To a solution of the noncyclized precursor polymer **5** (50 mg, 0.1 mmol) in dry chloroform (0.5 mL), trimethylsilyl iodide (1.0 mL of 0.5 M in chloroform, 0.5 mmol) was added dropwise at room temperature under nitrogen. This was left to stir at this temperature for 1 h, and a few drops of 1 M solution of NaOH were added to quench the reaction. The reaction mixture was extracted with chloroform and dried. The obtained solid was used without further purification, and was dissolved in dry dichloromethane (0.5 mL), followed by the addition of BBr₃ (0.5 mL of 1.0 M in dichloromethane, 0.5 mmol) at room temperature. The reaction mixture was further left to stir for 30 min at this temperature, and water was added. The organic layers were extracted and washed with water and methanol several times to give a bright yellow powder. This was further purified by a Soxhlet method using hexane as a solvent. The precipitate was collected and dried in vacuo to give the cyclized polymer **5a** as a bright yellow solid (25 mg, 50% over two steps); ¹H NMR (300 MHz, CDCl₃, δ) 7.8–7.7 (1H, br signal), 7.5–7.4 (1H, br signal), 6.9–6.7 (1H, br signal), 6.3–6.2 (1H, br signal), 5.1 (2H, br signal, 2 \times ArCH), 1.3–1.1 (20H, br signal), and 0.8 (6H, br signal); ν_{\max} (KBr)/cm⁻¹ 3037, 2997, 2927, 2851, 1635, 1463, 1443, 1208, and 1040.

4.1.1.3. Diethoxy terphenyl (10). A Schlenk tube containing a magnetic stirring bar was charged with Pd(PPh₃)₄ (88.3 mg, 0.057 mmol), compound **9** (0.40 g, 1.13 mmol), and K₃PO₄ (0.89 g, 4.20 mmol). The tube was evacuated and backfilled with nitrogen and then the pinacol ester of 2-hydroxyphenyl boronic acid **8** (0.50 g, 2.27 mmol) in degassed DMF (6.2 mL) was added. The mixture was stirred at 120 °C for 48 h under nitrogen. The reaction mixture was allowed to cool to room temperature and then was concentrated under reduced pressure. The mixture was extracted with CHCl₃ (3×20 mL) and the combined organic layers were washed with HCl (1 M; 20 mL), water (20 mL), brine (20 mL), dried over MgSO₄, and evaporated. The crude product was purified by column chromatography (3:1–2:1 hexane/EtOAc) to give **10** as a white crystal (0.18 g, 42%); mp 157–159 °C; *R_f* 0.33 (2:1 hexane/EtOAc); ν_{\max} (KBr)/cm⁻¹ 3427, 2976, 2927, 2854, 1638, 1482, 1443, 1382, 1351, 1287, 1226, and 1095; ¹H NMR (300 MHz, CDCl₃, δ) 7.36 (2H, s), 7.27 (2H, dd, *J*=7.5 and 7.5), 7.14 (2H, m), 7.01 (4H, dd, *J*=7.5 and 7.5), 6.66 (2H, br signal, 2×OH), 4.28 (4H, s), 3.47 (4H, q, *J*=6.5), and 1.17 (6H, t, *J*=6.5); *m/z* (FAB) 378 (M⁺, 20%), 149 (85%), and 57 (100%).

4.1.1.4. Silylation of 10 to afford 11. To a stirred solution of compound **10** (0.17 g, 0.46 mmol) in dry DMF (5 mL) was added *tert*-butyldimethylsilyl chloride (0.15 g, 1.01 mmol) at room temperature under nitrogen, followed by the addition of imidazole (94.4 mg, 1.38 mmol) and 4-di(methylamino)pyridine (2 mg, cat.). The mixture was stirred for 12 h, extracted with EtOAc (3×20 mL), washed with brine (20 mL), dried over MgSO₄, and evaporated. The crude product was purified by column chromatography (20:1 hexane/EtOAc) to give the product **11** as a white solid (0.22 g, 79%); mp 114–116 °C; *R_f* 0.45 (10:1 hexane/EtOAc); ν_{\max} (KBr)/cm⁻¹ 3070, 3028, 2957, 2927, 2890, 2857, 1601, 1574, 1482, 1443, and 1092; ¹H NMR (300 MHz, CDCl₃, δ) 7.34 (2H, s), 7.25 (2H, dd, *J*=7.5 and 7.5), 7.16 (2H, d, *J*=7.5), 7.02 (2H, dd, *J*=7.5 and 7.5), 6.90 (2H, d, *J*=7.5), 4.40 (4H, ABq, *J*=13.6, 2×ArCH₂), 3.30 (4H, q, *J*=7.0), 1.07 (6H, t, *J*=7.0), 0.75 (18H, br s), and 0.08 (12H, s); ¹³C NMR (125 MHz, CDCl₃, δ) 153.1, 137.3, 136.2, 133.1, 131.4, 129.2, 128.6, 121.4, 119.7, 70.1, 65.4, 25.6, 18.1, 15.4, and -4.0; *m/z* (FAB) 606 (M⁺, 5%) and 73 (100%).

4.1.1.5. Iodo benzyl sensory molecule (7). To a stirred solution of compound **11** (0.18 g, 0.29 mmol) in dry CHCl₃ (3 mL) was added 0.5 M trimethylsilyl iodide in CHCl₃ (1.18 mL, 0.59 mmol) at room temperature under nitrogen. The mixture was stirred for 1 h followed by the addition of methanol (5 mL) and water (5 mL), and was extracted with EtOAc (3×15 mL), washed with NaOH solution (1 M; 15 mL), brine (15 mL), dried over MgSO₄, and evaporated. The crude product was purified by column chromatography (20:1 hexane/EtOAc) to give the product **7** as a white solid (0.18 g, 80%); mp 166–168 °C; *R_f* 0.55 (10:1 hexane/EtOAc); ν_{\max} (KBr)/cm⁻¹ 3064, 3025, 2951, 2924, 2957, 1601, 1574, 1482, 1443, 1263, 1226, and 912; ¹H NMR (300 MHz, CDCl₃, δ) 7.32 (2H, dd, *J*=7.5 and 7.5), 7.19 (4H, br d, *J*=7.5), 7.08 (2H, dd, *J*=7.5 and 7.5), 6.92 (2H, d, *J*=7.5), 4.36 (4H, ABq, *J*=9.4, 2×ArCH₂), 0.75 (18H, br s, 2×SiC(CH₃)₃), and 0.13

(12H, s, 2×Si(CH₃)₂); ¹³C NMR (125 MHz, CDCl₃, δ) 152.7, 138.8, 137.4, 132.6, 131.8, 131.0, 129.4, 121.8, 119.9, 25.7, 18.2, 4.9, and -3.7; *m/z* (FAB) 770 (M⁺, 5%), 643 [(M-I)⁺, 35%], 516 (M-I₂)⁺, 35% and 73 (100%); [Found: (M-I)⁺ 643.1925. C₃₂H₄₄IO₂Si₂ requires *M*, 634.1925].

4.1.1.6. Cyclization of the indicator 7 to give 7a. Tetra-butylammonium fluoride (1 M in THF; 0.17 mL, 0.17 mmol) was added to a stirred solution of the silyloxy indicator **7** (60 mg, 0.078 mmol) in THF (1 mL) at room temperature under nitrogen. The mixture was allowed to stir for 5 min at this temperature. The reaction mixture was concentrated in vacuo and the residue was passed through a short plug of silica to give **7a** as a white solid (22 mg, 100%); mp 187–190 °C; *R_f* 0.38 (10:1 hexane/EtOAc); ν_{\max} (KBr)/cm⁻¹ 2957, 2923, 2853, 1731, 1603, 1490, 1451, 1234, and 1039; ¹H NMR (300 MHz, DMSO-*d*₆, δ) 7.88 (2H, d, *J*=7.5), 7.78 (2H, s), 7.30 (2H, dd, *J*=8.0 and 7.5), 7.11 (2H, dd, *J*=8.0 and 7.5), 7.00 (2H, d, *J*=7.5), and 5.20 (4H, s); ¹³C NMR (75 MHz, DMSO-*d*₆, δ) 154.3, 131.5, 129.7, 128.9, 123.5, 122.3, 122.1, 118.6, 117.1, and 67.5; *m/z* (FAB) 286 (M⁺, 20%), 285 [(M-1)⁺, 20%], 186 (75%), and 149 (100%); [Found: M⁺ 286.0994. C₂₀H₁₄O₂ requires *M*, 286.0994].

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 - The emission spectrum of the polymer **1a** was not obtained as the polymer was rarely soluble in most solvents attempted, and the fluorescence intensity of the prepared polymer **1a** was too low.
 - Cyclized polymers **1a** and **5a** displayed thermal stabilities up to 286 and 305 °C, respectively, after which temperatures continual weight loss was observed by TGA analysis. Further thermal and electrical properties of these novel polymers will be detailed elsewhere.
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 - Preparation of the ester polymer **1a** and its corresponding model compound **2a** was reported. See Ref. 8.