Chemosensing of nitroaromatics with a new segmented conjugated quaterphenylene polymer

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ABSTRACT

A new approach for introducing porosity in fluorescent polymer films to increase sensing performance is presented. A novel segmented conjugated polymer composed of *p*-quaterphenylene segments tethered by their meta positions along the polymer main chain by 2,2-isopropylene spacers was synthesized. The bent nature of its microstructure generates amorphous morphologies that let analytes diffuse rapidly within the films. Fluorescence quenching studies with polymer films and methanol solutions of nitroaromatics showed high sensitivity, fast response and reversibility of the fluorescence quenching. Thus, half of the maximum quench ($Q_{50\%}$) occurred with nitrobenzene at the micromolar range in less than 1 min in a reversible manner.

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Fluorescent polymers are functional materials with vast applications in organic optoelectronic devices such as light-emitting diodes,[1] solar cells,[2] electrochromic displays,[3] and fluorescent chemical sensors.[4] In particular, conjugated polymers (CPs), which possess a conjugated π-electron system delocalized along the polymer backbone, show inherent optoelectronic behavior differing markedly from the properties of their isolated repeating units. For example, CPs show increased sensitivity to fluorescence quenchers compared to small chromophores due to the diffusion of excitons throughout the individual polymer chains. This amplified response has led to an intense evaluation of CPs,[4] conjugated polyelectrolytes[4,5] as well as nanomaterials containing CPs[6] for sensing applications. Thus, CPs have been assessed as chemosensory materials for the detection and quantification of nitroaromatic compounds, a matter of importance in environmental pollution control, industrial applications, munitions remediation sites, and explosives detection.[4,7]

Most CPs have electron donor characteristics, therefore photoluminescence quenching by nitroaromatics, which follows the optical excitation that produces an electron–hole pair, is attributable to the electron-transfer quenching occurring from the excited polymer to the LUMO of the electron deficient nitroaromatic molecule. In addition, these nonbonding electrostatic interactions between a polymer and an analyte should be weak because a large association constant will otherwise result in irreversible responses or very long reset times. However, the sensing response of CP films does not only depend upon electronic factors but also on the way the analyte can physically interact with the CPs. Thus, the synthet-

ically laborious inclusion of three-dimensional ipticene moieties in poly(phenyleneethynylene)[8] main chains or [2,2,2] bicyclic ring moieties in poly(phenylenevinylene)s[9] or bulky [tris(alkyloxy-phenyl)methyl]phenyl groups in polycarbazole[10] keeps the polymer backbones apart and generates the porosity of molecular dimensions that let analytes diffuse rapidly within the films with the subsequent enhancement of their sensing performance.

We have been interested in developing new regularly segmented CPs, a subclass of CPs whose structures consist of non interacting[11–13] or weakly interacting[14,15] conjugated segments tethered along the main chain, usually by saturated spacers. Thus, we found that oligo(biphenylmethylene)s, where the spacer is a single saturated carbon atom, form amorphous glasses.[16] We have further extended our studies to a poly(terphenylenepropylene) segmented CP whose highly rigid and contorted structure also forms very stable disordered morphology with decreased segmental interactions.[17] The amorphous nature and high solubility of these materials suggested to us that efficient packing in the solid state is frustrated thus originating void space which could eventually foster analyte exchange with the media. Moreover, fluorescence depolarization measurements in oligo(biphenylmethylene)s films indicated that exciton migration by resonance energy transfer (RET) occurs in these disordered assemblies.[16] Therefore, it is conceivable that in the solid state the array of short conjugated segments could retain, at least in part, the amplified quenching effect of CPs. In this contribution we explore the quenching performance of quaterphenylene-based segmented CP films against nitroaromatics. We present the rather simple syntheses of a polymer composed of *p*-quaterphenylene segments tethered by their meta positions along the polymer main chain by 2,2-isopropylene spacers and its corresponding model compound (Scheme 1) along with their thermal and photophysical

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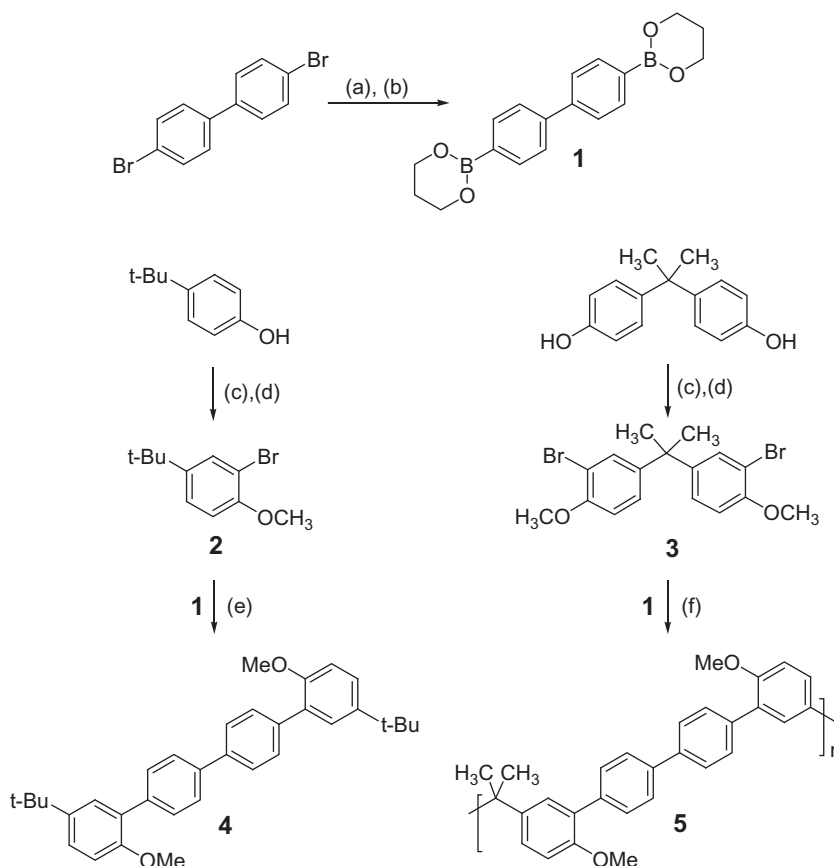
Scheme 1. Reagents and conditions: (a) BuLi/THF then B(OPr^i)$_3$ then H$_2$SO$_4$/H$_2$O, −78 °C; (b) 1,3-propanediol/toluene, reflux; (c) K$_2$CO$_3$/acetone then CH$_3$I, 35 °C; (d) Br$_2$/CH$_2$Cl$_2$, 4 °C; (e) Pd$_2$(dba)$_3$/P(*o*-tolyl)$_3$/CO$_3$Na$_2$ (aq)/THF, 80 °C (f) Pd(PPh$_4$)$_3$/CO$_3$Na$_2$ (aq)/THF, 80 °C.

properties. We then perform fluorescence quenching studies with amorphous films of the polymer and methanol solutions of some typical nitroaromatics.

The model compound **4** and polymer **5** were synthesized from readily available starting materials such as bisphenol A, their synthetic routes are illustrated in Scheme 1. The treatment of dibromobiphenyl with butyl lithium followed by triisopropylborate addition and acidification at a low temperature gave diboronic acid which was transformed into the diboronate **1** in an overall yield of 40%. The synthesis of **2** by dimethylation followed by dibromination was accomplished in 81% yield over the two steps. We have previously reported the preparation of **3** in 68% yield by the same synthetic procedure.[17] The bromides **2** and **3** were then used in the preparation of the model compound **4**[18] and polymer **5**[19] via palladium-catalyzed Suzuki condensations with **1**. Gel permeation chromatography (GPC, PS standards, THF) showed that **5** had a monomodal distribution (Mw = 7500 Da, PDI = 1.70) after reprecipitation from methanol. As expected, polymer **5** was readily soluble in common organic solvents such as acetonitrile, THF and DMF despite the absence of solubilizing chains. In particular, this polymer is highly soluble in CHCl$_3$ (50 wt %). Model compound **4** gives, after melting in a broad range around 150 °C, a kinetically stable amorphous phase (Tg = 51 °C) while polymer **5** is amorphous in nature; its DSC traces registered at a temperature range between 50 and 300 °C showed only a distinct glass transition at 161 °C and no melting transitions were found upon heating beyond the glass transition temperature. Besides, no birefringence was detected for **5** by polarized optical microscopy POM observations carried out in the same temperature range. Films cast on quartz plates and dried under vacuum gave smooth films suitable for optical measurements.

The absorption and emission spectra of **4** and **5** are shown in Figure 1 for both samples in dilute solution and neat films. The corresponding photophysical data are reported in Table 1. Altogether, the methoxy and alkyl substituents cause a ≈14 nm red-shift in their absorption and emission peaks compared to those of *p*-quaterphenyl[15] and the photophysical properties of the model compound are mirrored in the polymer. Little distinction can be made in the optical and fluorescence spectra in dilute chloroform solutions (Fig. 1a) between **4** and **5**, indicating that the isopropylene spacer indeed isolates the conjugated segments electronically along the backbone. In addition, both **4** and **5** have comparable molar (per repeating unit) absorption coefficients and fluorescence quantum yields (see Table 1), whose considerable magnitudes indicate that they retain the excellent photophysical properties of the *p*-quaterphenyl chromophore. Thus, from the observed similarity in the optical and photophysical properties a regular microstructure of **5** constituted of well-defined noninteracting chromophores can be inferred. Although there are no distinctive differences between the absorption spectra of neat films of **4** and **5**, the corresponding fluorescence spectra show discrepancies at the low energy edge (Fig. 1b). The spectrum of **4** presents a broader full width at half-maximum, *f*whm, and has a noticeable red tail that is absent in the spectrum of **5**. Thus, it is likely that spectral broadening is a result of interchromophoric contacts which are not completely impeded by *tert*-butyl disubstitution in the elongated quaterphenylene model compound. Apparently, the geminal substitution in the polymer backbone, which forces the chromophores into an angular disposition producing a contorted polymer microstructure, succeeds in removing segmental interactions so that the solution and the film fluorescence spectra of **5** are quite similar. Monoexponential decay curves of the luminescence were
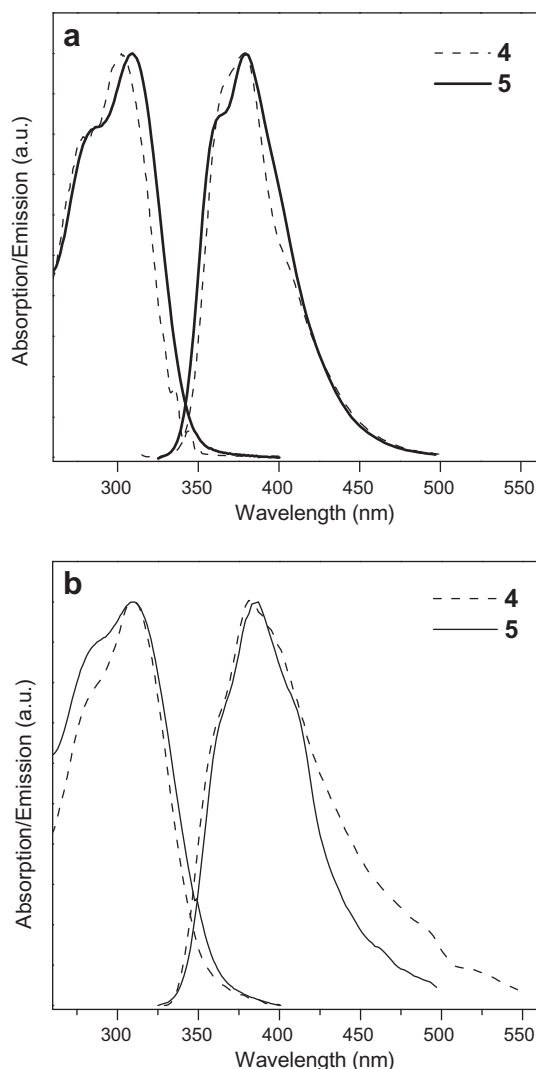
Figure 1. (a) Normalized absorption and emission spectra for **4** (dashed curves) and **5** (solid curves) measured as (a) dilute solutions in CHCl$_3$ or (b) neat films on quartz.

Table 1

Photophysical properties of model compound **4** and polymer **5** measured from CHCl$_3$ solutions and thin neat films

	Media	Absorption	Fluorescence		SS[d]	Φ_F[e]	τ_f[f]	‹r›[g]
		$\lambda_{max}(\varepsilon_{max})$[a]	λ_{max}[b]	f_{whm}[c]				
4	CHCl$_3$	306 (29500)	366, **378**	48	72	0.91		
	Film	310	360, **384**	86	74		0.13	0.192
5	CHCl$_3$	309 (28700)	**379**	50	70	0.72		
	Film	306	**387**	65	81		0.25	0.271

[a] Absorption maxima measured in dilute CHCl$_3$ solutions and on films and extinction coefficients (based upon the molar repeating unit for **5**) in M^{-1}cm^{-1}.

[b] Emission maxima measured in dilute CHCl$_3$ solutions and on films (λ_{exc} = 310 nm). Bold data indicate the major peaks.

[c] Full width at half-maximum of the fluorescence bands (in nm).

[d] Stokes shifts in dilute CHCl$_3$ solutions and on films ($\lambda_{max,em}$ - $\lambda_{max,abs}$; in nm).

[e] Fluorescence quantum yields measured in CHCl$_3$ (λ_{exc} = 310 nm).

[f] Observed lifetime at $\lambda_{max,em}$ = 400 nm on thin films (in ns).

[g] Average anisotropy measured in thin films (λ_{exc} = 335 nm) in an emission range of 60 nm around the $\lambda_{max,em}$.

observed in the films of **4** and **5** which showed lifetimes of the single-chromophore excited states in the same range. The steady-state anisotropies which indicate energy migration were likewise comparable. Finally, a film sample of **5** showed before and after

thermal annealing (6 h, N$_2$, 170 °C) the same fluorescence spectra and anisotropy values (0.271 vs 0.268), corroborating that the amorphous morphology of **5** is quite stable.

The steady-state fluorescence response of polymer **5** films to increasing concentrations of various analytes was observed for methanol solutions of nitrobenzene (NB), 4-nitroaniline (NA), 1,3-dinitrobenzene (DNB), 2,4-dinitrofluorobenzene (DNFB), trinitrotoluene (TNT), picric acid (PA) and nitropropane (NP). Contamination of the analysis systems by polymer leaching is always a concern for sensing configurations consisting of films immersed in a liquid medium.[20] In our case, control experiments confirmed the structural stability of polymer **5** films; no fluorescence was detected in methanol that soaked films for 12 h and the fluorescence intensity of pristine films did not decrease after such immersion period. We observe instead that wet films increase 25–30% of the fluorescence intensity reaching a maximum steady value in few minutes. Figure 2a shows the fluorescence intensity of **5** as a function of added NB. The fluorescence intensity was recorded first in neat methanol, I_o, and then after the quencher solution was added, I. The film response was rapid, that is, steady fluorescence intensity was always reached in ca. 40–50 s after the addition of an aliquot of the quencher solution, indicating that fast diffusion of the analyte within the film must occur in order to readily attain its film/
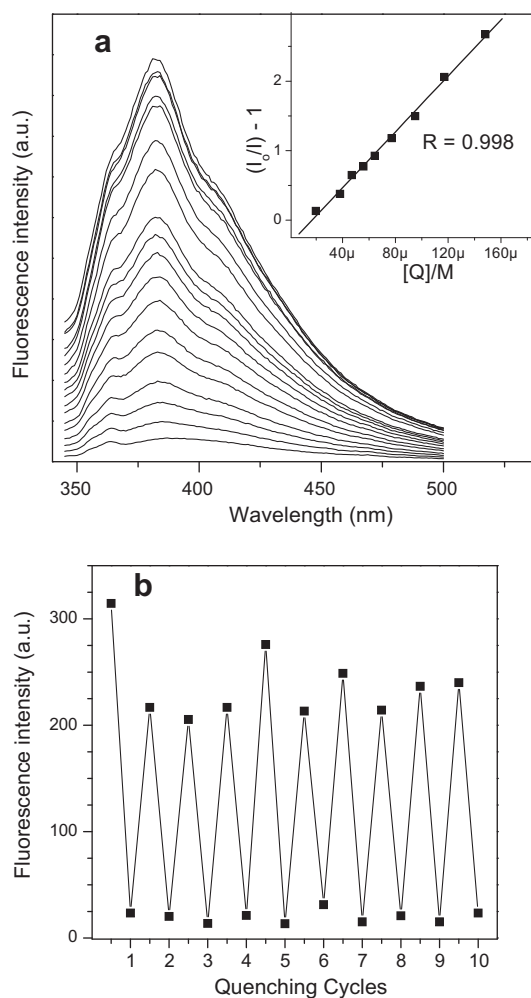

Figure 2. (a). Fluorescence spectra change of **5** film as a function of an added NB in MeOH; [NB] = 6.0 10^{-6}–3.8 10^{-4} M (top to bottom). The corresponding Stern–Volmer plot is shown in the inset including the correlation coefficient for the linear fit. (b) Ten continuous cycles of quenching-recovery test of **5** film. The quenching was measured after exposing the film to [NB] = 4.3 10^{-3} M for less than 1 min.

solution distribution ratio. The plot of the Stern–Volmer (S–V) equation, $(I_o/I) - 1 = K_{SV}[Q]$, for fluorescence quenching shown in Figure 2a (inset) indicates that **5** has a considerable sensitivity towards NB. Thus, half of the maximum quench, $Q_{50\%}$, that is, the quencher concentration needed to reach $(I_o/I) - 1 = 1$, of **5** with NB occurred at the micromolar range ([NB] = 64 μM) while almost complete quenching ($Q_{10\%}$) was achieved with a 300 μM solution. A linear relationship was observed between 10% and 70% of fluorescence quenching with a S–V constant (K_{SV}) of 2.01 10^4 M^{-1}; a value higher than those observed for conjugated polymers in solution,[21,7] where diffusion of the analyte is not hindered. However, at higher quencher concentrations a nonlinear S–V relationship with upward curvature occurred. Similar upward deviations from linearity have been observed in other solid/solution sensing configurations.[22] The reversibility of the sensing response was also examined. Figure 2b shows ten continuous cycles of fluorescence quenching-recovery using NB as an example nitro aromatic compound which indicate that quenching is intrinsically reversible. In these experiments, a quencher solution was employed to quench the film fluorescence, next the quencher solution was withdrawn, the film was washed with methanol and its fluorescence was recorded, then measurements in the presence and absence of the analyte were repeated several times (each cycle took nearly 6 min). Thus, fast fluorescence response equilibration and reversible quenching evidenced that the amorphous morphology of the segmented conjugated polymer **5** has porosity of molecular dimensions and therefore analytes can rapidly diffuse in and out of the films.

Figure 3 shows representative S–V plots for **5** with the different analytes tested. TNT was not included because no fluorescence quenching was observed for this analyte. Overall, the data appear linear up to 50–70% of the fluorescence quench, and then upward curving of the S–V plots take place for all nitroaromatics employed in this study. The data from the linear range could be fitted with correlation coefficients above 0.994 for all fittings and the values of K_{SV} determined from the slopes are listed in Table 2.

It can be observed that efficiency in fluorescence quenching follows the order of NA > PA > NB ≫ DNFB > DNB ⋙ TNT. Although the trend in S–V constants usually reflects the electron acceptor ability of the quencher, for example, TNT > DNT > NT,[8] the films of polymer **5** exhibit on the whole a quenching efficiency which seem to reflect a combination of the steric and electronic characteristics of the analyte as well as the occurrence of noncovalent interactions between polymer and analyte. We noted that larger
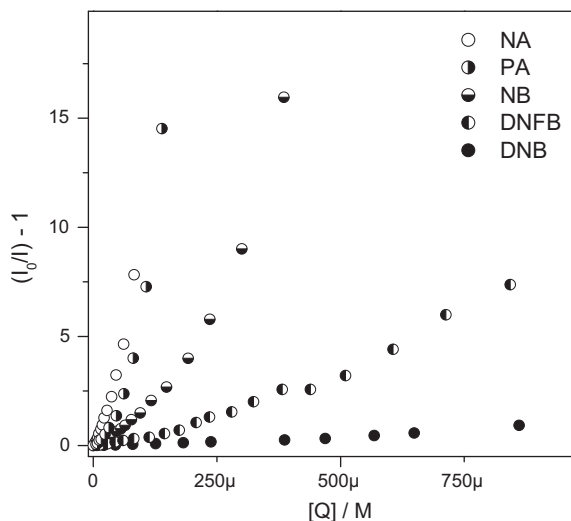
Table 2
Comparison of quenching efficiencies

Quencher (Q)	K_{SV}, M^{-1}.	$Q_{50\%}$, μM[a]
NA	64100	18
PA	32000	37
NB	20100	64
DNFB	4000	240
DNB	610	860

[a] [Q] for $(I_o/I) - 1 = 1$.

responses were observed with NA and PA that can interact by hydrogen bonding with the methoxy groups of the polymer. An alternate explanation for the relatively large response of NA and PA is that they are nonfluorescent molecules which absorb near the polymer emission range and act as acceptors for the RET from the excited polymer, thus opening another channel for fluorescence quenching. In addition, it would seem that the access of larger compounds into the film is difficult or obstructed as in the case of TNT. These results highlight the difficulties already encountered in establishing definitive trends for quenching responses in condensed state.[8,20,23] In summary, a new approach for introducing porosity in fluorescent polymer films to increase sensing performance was presented. A quaterphenylene-based segmented conjugated polymer was synthesized using an unsophisticated synthetic route. The chromophores are tethered by their meta positions along the polymer main chain by 2,2-isopropylene spacers which force them into an angular arrangement and produce a contorted polymer microstructure. We attribute the high sensitivity and fast reversible response of the fluorescence quenching by nitroaromatics to the amorphous morphology of the polymer as well as to the exciton migration by RET that occurs in these disordered assemblies of the chromophores.

Acknowledgments

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.07.055.

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Figure 3. Stern–Volmer plots of **5** in response to nitro compounds.

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18. Synthesis of 2,2‴-dimethoxy-5′,5‴-diterbutyl-4,1′:4′,1″:4″,1‴-quaterphenyl (**4**). A Schlenk tube was charged with diboronate ester **1** (0.20 g, 0.62 mmol), bromide **2** (0.35 g, 1.36 mmol), Pd₂(dba)₃ (2 mg, 1.2 μmol), P(o-tolil)₃ (2 mg, 7 μmol), Na₂CO₃ (0.89 g, 8.25 mmol) and the mixture was kept under Ar atmosphere. Dry THF (3.3 mL) and water (3.3 mL) were added via a syringe. The mixture was heated at 80 °C for 48 h, then poured into MeOH (15 mL), extracted with CHCl₃ (3 × 15 mL) and dried with SO₄Na₂. The solvent was removed and the resulting solid was recrystallized from ethanol.(0.11 g, 38%). Mp = 148–151 °C. ¹H NMR – (CDCl₃): = 7.69 (d, 2H, J_o = 8.58 Hz), 7.63 (d, 2H, J_o = 8.58 Hz), 7.40 (d, 1H, J_m = 2.67 Hz), 7.34 (dd, 2H, J_o = 8.58 Hz, J_m = 2.67 Hz), 6.94 (d, 1H, J_o = 8.58 Hz), 3.83 (s, 3H), 1.36 (s, 9H). ¹³C NMR: 31.6, 34.2, 55.7, 110.9, 125.2, 126.8, 128.1, 129.7, 129.9, 138.0, 139.6, 143.6, 154.4. C₃₄H₃₈O₂ (478.66): C, 85.31; H, 8.00. Found: C, 85.08; H, 7.93.

19. Synthesis of Poly(2,2‴-dimethoxy-4,1′:4′,1″:4″,1‴-quaterphenyl-5,5‴-ylene)propylene (**5**). A Schlenk tube was charged with Pd(PPh₃)₄ (0.44 g, 0.38 mmol), diboronate ester **1** (0.540 g, 1.67 mmol), dibromo **3** (0.70 g, 1.67 mmol), Na₂CO₃ (2.82 g, 26.6 mmol) and and the mixture was kept under Ar atmosphere. Dry THF (13.3 mL) and water (13.3 mL) were added via a syringe. The mixture was heated at 80 °C for 7 days. The reaction mixture was then poured into methanol (30 mL). The precipitate was dissolved in CHCl₃ (5 mL) and poured into methanol (30 mL). The procedure was repeated twice. The precipitate was collected and dried under vacuum to yield **5** as a yellowish powder (0.63 g, 92%). ¹H NMR (CDCl₃): = 7.63 (m, 4H), 7.37 (d, 1H, J_m = 2.48 Hz), 7.26 (dd, 1H, J_o = 8.70 Hz, J_m = 2.48 Hz), 6.91 (d, 1H, J_o = 8.70 Hz), 3.84 (s, 3H), 1.72 (s, 3H). ¹³C NMR (CDCl₃): = 154.5, 143.2, 139.5, 137.8, 132.0, 130.0, 129.4, 127.3, 110.8, 55.6, 41.9, 31.2. Anal. Calcd for (C₂₉H₂₆O₂)ₙ (406.5)ₙ: C, 85.68; H, 6.45. Found: C, 85.19; H, 6.14.

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