

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/46576553>

# Highly Sensitive and Selective "Turn-on" Calcium Cation Sensing from a Dendronic Terthiophene Tetraethylene Glycol (TEG) Molecule

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · OCTOBER 2010

Impact Factor: 3.3 · DOI: 10.1021/jp1068522 · Source: PubMed

---

CITATIONS

11

READS

25

## 4 AUTHORS, INCLUDING:



Dahlia C. Apodaca  
Mines and Geosciences Bureau  
9 PUBLICATIONS 122 CITATIONS

[SEE PROFILE](#)



Rigoberto C. Advincula  
Case Western Reserve University  
334 PUBLICATIONS 7,238 CITATIONS

[SEE PROFILE](#)

# Highly Sensitive and Selective “Turn-on” Calcium Cation Sensing from a Dendronic Terthiophene Tetraethylene Glycol (TEG) Molecule

Yushin Park, Dahlia C. Apodaca, Jonathan Pullen, and Rigoberto C. Advincula\*

Department of Chemistry and Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204-5003, United States

Received: July 22, 2010; Revised Manuscript Received: September 7, 2010

A molecule consisting of a branched or dendritic terthiophene with tetraethylene glycol moiety (**3T5O**) was synthesized for highly sensitive and selective calcium ion detection in solution. The sulfur atoms of the terthiophene dendron moiety contribute to the metal–ligand complexation of calcium cations. The modification of the terthiophene dendrons with a hydroxyl-terminated tetraethylene glycol (TEG) group produces a twisted intramolecular charge transfer (TICT) event in which the terthiophene moiety is conformationally twisted, affecting its chromophoric and fluorophoric activity. This twisted conformation resulted in an increase in emission intensity at 320 nm, at the same time producing a blue shift in the absorption spectra. This process enabled a “turn-on” system for calcium ion detection compared to most “turn-off” systems involving a quenching route. The intensity of the emission is related to saturation of the terthiophene moiety at a concentration of **3T5O**:[Ca<sup>2+</sup>] 1:4, of  $\sim 1 \times 10^{-8}$  M, which indicates high sensitivity for calcium cations. No response with other cations such as Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup> was observed, which also indicates high selectivity for the system. Conformational analysis of the **3T5O** and the twisted terthiophene dendron geometry was done by semiempirical PM3 modeling. In an effort to distinguish specific interactions between monovalent and divalent cations and the **3T5O**, restricted Hartree–Fock level calculations using the STO-3G basis set were also performed. The calculations correlated with the experimental results.

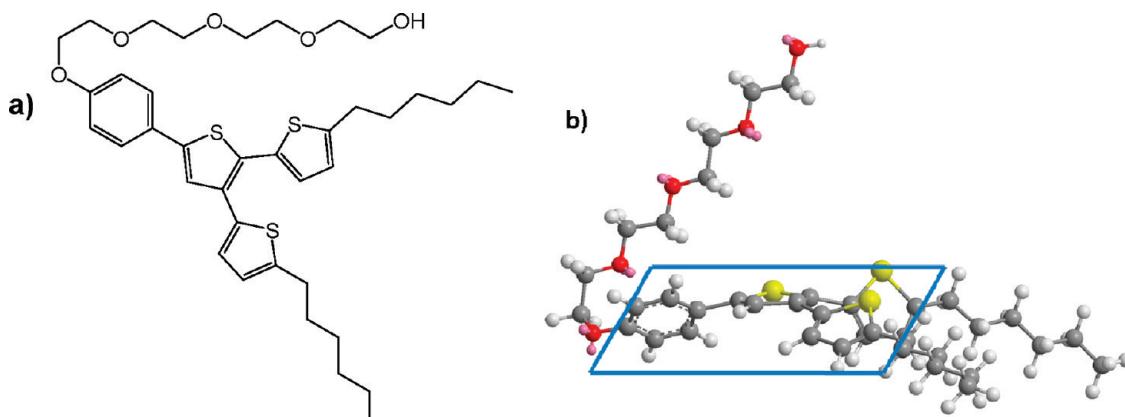
## Introduction

Synthesizing sensitive and selective chemosensors for specific analyte detection is an interesting topic due to challenges in molecular design and its applications in a number of research fields.<sup>1</sup> Moreover, the detection of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> cations using various chromophoric moieties under physiological or buffered conditions is an active field in chemistry, biology, and medicine.<sup>2–6</sup> In addition, a sensing system that detects calcium cations in the presence of sodium or potassium cations is important since calcium cations trigger, regulate, and influence a number of physiological processes.<sup>7,8</sup> Most well-known ion-detecting materials usually consist of ring-structured moieties such as crown ethers,<sup>9–11</sup> cyclodextrins,<sup>12,13</sup> and calixarenes.<sup>14–16</sup> In particular, the binding event between ether moieties in crown ether derivatives and cations is essential for any sensing study. Due to the size-dependent specific interaction with cations, crown ether derivatives have been applied widely in biochemistry and environmental science. Recently, ethylene glycol oligomeric derivatives have been reported for ion sensing. The twisted ethylene glycol moieties act similarly to crown ethers making complexes with cations at specific sizes.<sup>17,18</sup> Calcium ion specific detecting sensors have been synthesized by de Silva et al. that utilized photoinduced electron transfer (PET).<sup>19</sup> A typical design for these chemosensors involves a conformation change that allows greater  $\pi-\pi$  stacking to occur, resulting in the occurrence or extinction of chromophores which produce different optical outputs. These output signals from the binding event are achieved by an energy- or charge-transfer process that occurs while the supramolecular stacking properties of the chromophore are altered.<sup>2,7</sup> Normally, self-quenching of flu-

rescence or “turn-off” is observed when the cation detection causes structural changes from monomers to excimers.<sup>3,4a,20</sup> In addition, ionic bonds between cations and sensing molecules can change the intramolecular structure of chromophores. However, this “turn-off” system could lead to poorer sensitivity for the reason that many conjugated polymers are prone to fluorescence quenching brought about by aggregation due to chromophore–chromophore interactions.<sup>45</sup> Changes in the emission intensity would therefore be attributed to both sensing of the ions and aggregation. Also, chemosensors based upon photoinduced electron transfer (PET) often exhibit anomalous emission properties displaying poor selectivity due to interference of related cations.<sup>46</sup> On the other hand, with this “turn-on” sensing of calcium ions, sensitivity and selectivity are greatly improved with the use of a terthiophene dendron containing the TEG group. Apart from the expected twisting on the conformation of the terthiophene units resulting in dual fluorescence, the encapsulation of calcium ion by the hydroxyl TEG moiety provides enhancement on both the absorption and emission peaks brought about by a strong ionic bond and strong ion dipole electrostatic forces of attraction between the calcium cation and negative dipoles of the oxygen atoms of the TEG moiety.

Nakamura and co-workers reported the detection of calcium cations and alkali earth metal ions from a twisted intramolecular charge transfer (TICT) behavior by fluorescence.<sup>21</sup> The TICT model was capable of explaining dual fluorescence along with the large Stokes shift of the emission bands of *p*-(*N,N*-dimethylamino)benzonitrile in a polar solvent.<sup>22</sup> In another study by Hu et al.,<sup>55</sup> an examination was made to determine the effect of temperature on the TICT process. It was reported that the emission of a TICT luminogen is sensitive to temperature variations. Results would show that by varying the temperature

\* To whom correspondence should be addressed. Phone: 713-743-1760. E-mail: radvincula@uh.edu.



**Figure 1.** (a) Chemical structure of the dendron **3T5O** with (b) a ball–stick model highlighting the planar region of the chromophore sensor.

from  $-75$  to  $60$  °C, a continuous increase in the emission intensity accompanied by a gradual blue shift in the emission maximum was observed. Since then, the TICT model has been used to explain other dual fluorescence properties with similar chemicals.<sup>23,24</sup> This model was also used to elucidate the “off–on” fluorescence output mechanism of 1-pyrenyl aromatic amides.<sup>21</sup> However, in order to utilize this model efficiently, the complex formed between sensing materials and cations needs to be designed carefully and parametrized.<sup>22a</sup>

There are limited compounds that possess dual fluorescence which can be used as molecular probes to sense changes in the microscopic microenvironment. A signaling unit which produces a sufficiently strong and specific spectroscopic change is an essential criterion for designing chemosensors in solution.<sup>25</sup> The molecule shown in Figure 1 was designed and targeted to assemble incremental changes in absorbance and fluorescence activity in the presence of calcium cations. Normally, when the primary chromophores are within a highly  $\pi$ -conjugated system, the other end group is modified with a different conjugated system that develops  $\pi$ – $\pi$  stacking. For example, it has been reported that poly(*p*-xylylene) moieties enable metal–ligand cross-linking with metal ions.<sup>26</sup> In our case, the thiophene dendron was modified with the TEG moiety to facilitate ion capture. Recently, thiophene dendrons were synthesized in our group due to their strong absorption properties in the  $250$ – $400$  nm wavelength region. Another interesting feature of these dendrons is the light-harvesting and energy-transfer properties when synthesized as an antenna macromolecule.<sup>27</sup> The thiophene dendron moiety exhibits ( $\alpha,\beta$ -linkage) which breaks the conjugation and allows a blue-shifted absorption compared to a linear thiophene ( $\alpha,\alpha$ -linkage). However, this dendron sensor was also designed to allow the hydroxyl-terminated TEG group to play an important role for cation trapping together with the thiophene dendron moieties. The manifested sensitivity of the hydroxyl-terminated TEG group is then expected to give rise to an emission peak appearing at lower energy. On the other hand, by adding a phenyl ring between the TEG and thiophene dendrons, the sulfur atoms in the thiophene dendrons can properly contribute to the interaction event with the cations, which is then detected through twisting of the thiophene conformation. Both these phenomena give rise to dual fluorescence via a TICT. Furthermore, high sensitivity and selectivity was observed for this sensing system compared to what can be achieved if the TICT system were attempted on a one-dimensional or linear  $\pi$ -conjugated oligothiophene system alone. The expected sensitivity via this TICT mechanism is not greatly affected by the saturation of  $\text{Ca}^{2+}$  ions that bind with the thiophene dendron due to the possibility of dimer formation

in solution which would then require more  $\text{Ca}^{2+}$  ions before saturation can be reached.<sup>53</sup> Each emitting molecule may assume a different twisted molecular conformation depending on the following factors: (1) solvent effects; (2) substitution on the side chain of the thiophene dendron which could affect the regioregularity of the polymer backbone; (3) diameter of the cation; (4) number of ligand binding sites; and (5) the relative cation to ligand cavity size ratio. It is highly probable that each factor may counteract each other. The extent of which may be translated to different absorption and emission characteristics.<sup>55</sup>

Along with this sensing via TICT state, the solvating power of the solvent to stabilize the twisted molecular conformation can intensify both absorption and emission with incremental changes on the concentration of the calcium ions. The correctness of this molecular design is validated by our experimental results and the semiempirical calculations as described in this paper.

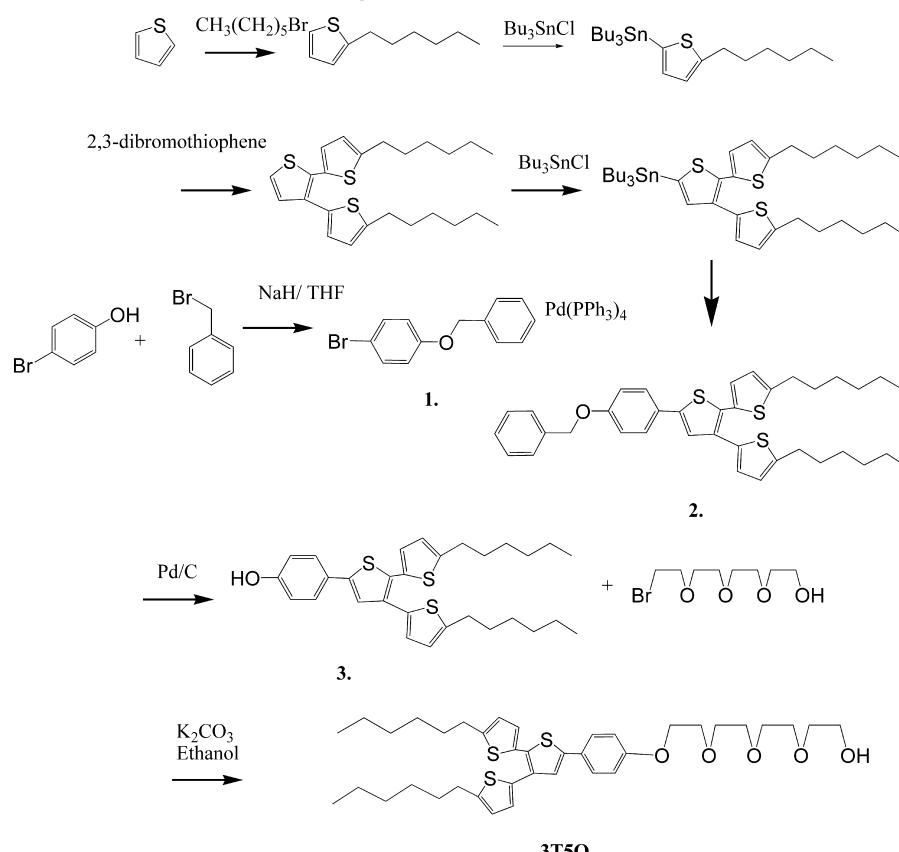
## Experimental Section

**General Methods.** All chemicals were purchased from Aldrich Chemical Co. and were used directly without further purification. Tetrahydrofuran (THF) was freshly distilled over sodium and benzophenone before use. All solvents were aspirated with nitrogen gas before use.

**Synthesis.** The chemosensor molecule was prepared by etherification of a thiophene dendron (G-1) possessing phenol groups at their focal point with brominated ethylene glycol (**3T5O**) (Scheme 1). The 2,3-dibromothiophene has proven to be a very useful  $\text{AB}_2$  monomer for the formation of poly-thiophene dendrimers.<sup>27</sup> The tetraethylene glycol was chosen as a binding unit to interact with calcium cations. The hydroxyl group at the end of TEG is present to increase the possibility for ionic bonding or amphiphilicity. The absence of a phenyl ring prevents the formation of a twisted structure of the chromophore moiety as will be discussed later with the calculations. Terthiophene dendrons ( $\alpha,\beta$  linkage) were used as the signaling unit to break the  $\pi$ -conjugation in a linear terthiophene (all  $\alpha,\alpha$  linkage). This combination produces a “turn-on” sensing system.

**Thiophene Dendron ( $\alpha,\beta$  Linkage) Synthesis.** The synthetic protocol for terthiophene dendron (tributyl(5,5''-dihexyl-[2,2';3',2'']terthiophene-5'-yl)stannane) is included in Scheme 1. Our group reported the procedure for terthiophene dendrons previously.<sup>27b</sup>

**Synthesis of 1-((4-Bromophenoxy)methyl) (**1**).**  $1.2$  g of sodium hydride was added slowly to a solution of 4-bromophenol ( $5$  g) in tetrahydrofuran with stirring at  $0$  °C. After  $30$  min,

**SCHEME 1: Synthesis of Calcium Cation Detecting Sensor**

1.2 g of benzyl bromide was added dropwise under nitrogen atmosphere. Then, the reaction was allowed to warm to room temperature overnight. The mixture was stirred with water to kill excess of sodium hydride. After drying the mixture under vacuum, it was extracted with methylene chloride. The product was purified with silica gel column chromatography. 4.8 g of pure product was obtained (yield: 63%).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ):  $\delta$  7.33–7.42 (m, 7H), 6.85 (d, 2H), 5.04 (s, 2H).

**Synthesis of 1-((4-Bromophenoxy)methyl)-4-(5,5''-dihexyl-[2,2';3',2'']terthiophene-5'-yl)benzene (2).** 1.3 g of tributyl(5,5''-dihexyl-[2,2';3',2'']terthiophene-5'-yl)stannane, 0.5 g of 1-((4-bromophenoxy)methyl), 50 mg of tetrakis(triphenylphosphine)palladium, and a catalytic amount of CuI was dissolved in DMF under an inert atmosphere and refluxed overnight. The mixture was cooled down to room temperature and DMF was removed under vacuum. After simple extraction, the product was purified with silica gel column chromatography. 0.5 g of pure product was obtained (yield: 50%).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ):  $\delta$  7.52 (d, 2H), 7.36–7.41 (m, 5H), 7.20 (s, 1H), 6.95 (d, 1H), 6.90 (d, 1H), 6.85 (d, 2H), 6.67 (d, 2H), 5.10 (s, 2H), 2.74–2.81 (td, 4H), 1.60–1.66 (m, 4H), 1.25–1.40 (m, 12H), 0.88 (t, 6H).

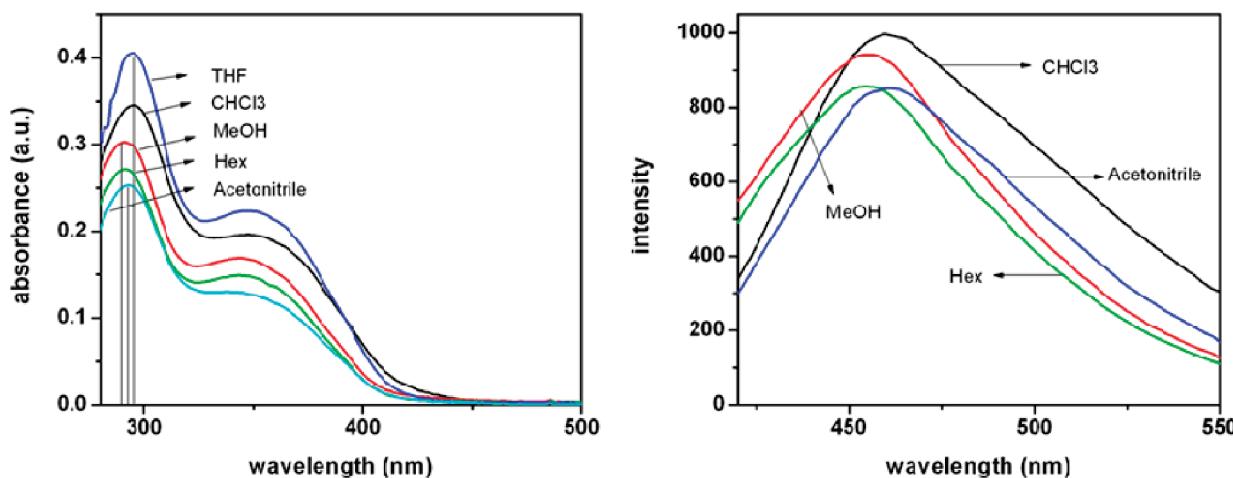
**Synthesis of 4-(4,5-Bis(5-hexylthiophen-2-yl)thiophen-2-yl)phenol (3).** 0.8 g of compound 2 was dissolved in a cosolvent of methanol and methylene chloride followed by a 10% activated Pd/C suspension. Then, hydrogen gas was bubbled into the solution at room temperature for 2 days. The mixture was filtered to remove Pd/C and the compound was purified with silica gel column chromatography. 0.4 g of pure product was obtained (yield: 50%).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ):  $\delta$  7.46–7.49 (d, 2H), 7.20 (s, 1H), 6.94 (d, 1H), 6.89 (d, 1H), 6.84–6.86 (d, 2H), 6.67 (d, 2H), 2.74–2.81 (td, 4H), 1.60–1.66 (m, 4H), 1.25–1.40 (m, 12H), 0.88 (t, 6H).  $^{13}\text{C}$  NMR (in  $\text{CDCl}_3$ ):  $\delta$  155.75, 151.88, 151.39, 147.70, 146.10, 142.13, 138.41, 135.78, 127.61, 127.51,

125.14, 124.41, 123.33, 116.28, 116.19, 31.98, 31.91, 30.56, 30.52, 29.15, 23.05, 22.98, 14.49.

**Synthesis of 5-(4-(2-(2-(4,5-bis(5-hexylthiophen-2-yl)thiophen-2-yl)phenoxy)ethoxy)ethoxy)ethoxyphenyl)-2,3-bis(5-hexylthiophen-2-yl)thiophene (3T5O).** 0.2 g of compound 3, 57 mg of 2-(2-(2-bromoethoxy)ethoxy)ethoxyethanol, and 54 mg of potassium carbonate were dissolved in ethanol and refluxed overnight. The mixture was dried under vacuum and simply extracted with methylene chloride. The compound was purified with silica gel column chromatography. 0.2 g of pure product was obtained (yield: 44%).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ):  $\delta$  7.5 (d, 4H), 7.20 (s, 2H), 6.94 (d, 2H), 6.89 (d, 2H), 6.84–6.86 (d, 4H), 6.67 (d, 4H), 4.17 (d, 4H), 3.88 (d, 4H), 3.68–3.74 (m, 6H), 3.62 (d, 2H), 2.74–2.81 (td, 4H), 1.60–1.66 (m, 4H), 1.25–1.40 (m, 12H), 0.88 (t, 6H).  $^{13}\text{C}$  NMR (in  $\text{CDCl}_3$ ):  $\delta$  158.92, 147.66, 142.18, 135.37, 132.90, 132.55, 132.42, 128.97, 128.81, 127.58, 127.22, 126.51, 125.14, 124.53, 124.41, 115.40, 72.91, 71.22, 71.05, 70.98, 70.71, 70.09, 67.89, 62.16, 31.98, 31.91, 30.56, 30.52, 29.15, 23.05, 22.98, 14.49. Anal. Calcd for  $\text{C}_{38}\text{H}_{52}\text{O}_5\text{S}_3$ : C, 66.63; H, 7.65. Found: C, 66.43; H, 7.77. Exact mass calculated for  $[\text{C}_{38}\text{H}_{52}\text{O}_5\text{S}_3]^+$  requires  $m/z$  684.30; found, 684.46.

**Results and Discussion**

**Absorption and Fluorescence Spectroscopy of 3T5O.** The absorption spectrum of 3T5O shows a strong peak around 300 nm, representing the terthiophene dendron ( $\alpha,\beta$  linkage) moiety. A smaller band around 350 nm, with half the intensity of the primary band at 300 nm is due to the conjugation of the phenyl and terthiophene dendron in solution (Figure 2). By contrast, a linear terthiophene ( $\alpha,\alpha$  linkage) has absorbance at 345 nm and emission at 435 nm (345 nm excitation).<sup>28</sup> Linear terthiophenes



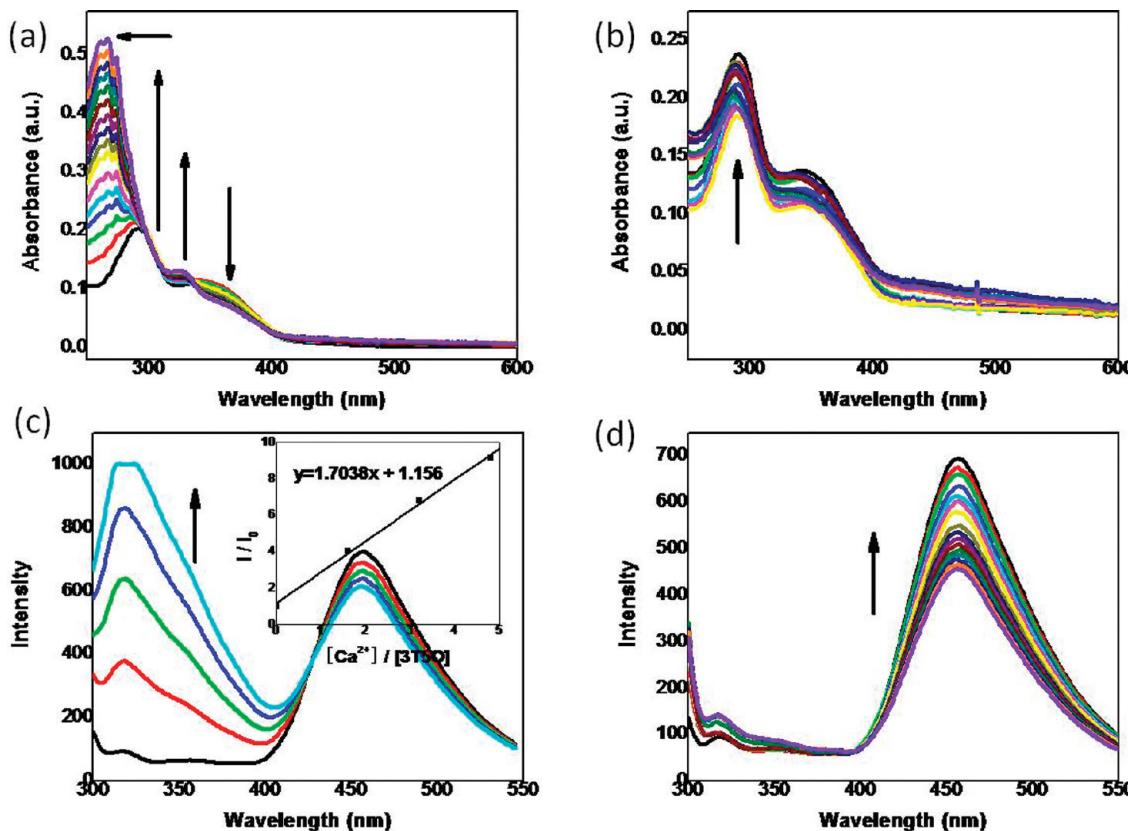
**Figure 2.** Absorbance and emission spectra of **3T5O**: (a) UV spectrum ( $b = 1\text{ cm}$ ) and (b) fluorescence which was excited at 300 nm and 350 nm in hexane,  $\text{CHCl}_3$ , THF, methanol, and acetonitrile (emission and excitation slit widths = 10 nm).

are also strongly aggregated.<sup>29</sup> A solvatochromic effect on the absorption spectra was observed due to the amphiphilic property of **3T5O**. As a result, the absorption and fluorescence shifts varied with the structural conformation of **3T5O**, which consequently gives an approximation on the relative solvating power of the solvent. Amphiphilic polythiophenes such as **3T5O** exhibit a much lower hydrodynamic volume indicating a more compact conformation in THF than in chloroform<sup>47</sup> hence a relatively higher  $\lambda_{\text{max}}$  as shown in Figure 2a. Molar absorbance was calculated at  $\epsilon = 10\,000\text{ L mol}^{-1}\text{ cm}^{-1}$  at 300 nm and  $\epsilon = 5416.7\text{ L mol}^{-1}\text{ cm}^{-1}$  at 350 nm in THF solution. On the other hand, it is presumed that the blue shift observed in hexane may be due to the strongly polar character of the hydroxyl-terminated TEG group of the emitting state of **3T5O**. The intermolecular interactions of the strongly polar character of the side chain eliminates the internal energy barrier even in the presence of a nonrelaxing, rigid property in hexane, resulting in an increase in the population of the charge-transfer state.<sup>48</sup> While this was the assumption for the observed red shift in hexane, it is believed that the twisted conformation of the terthiophene units coupled with the electrostatic interaction of the calcium ion with the TEG group may have effectively counteracted interaction of the solvent molecules with the dendron units. This could provide a favorable complexation enthalpy to cause the desired complexation between the dendron and the metal ion. This eventually leads to a shift in the emission  $\lambda_{\text{max}}$  toward the blue region. However, only a single emission band at 460 nm was seen when the solution was excited at both 300 and 350 nm. The single emission indicates a larger conjugation between the terthiophene dendron and the phenyl ring, i.e., energy transfer from the terthiophene dendron moiety to the phenyl group resulting in a single emission. It should be noted that the presence of a single emission a priori is important in the context of how, by disrupting the planar conformation of this molecule, a second higher energy emission is eventually observed. Hence, it may be generalized that molecular twisting of the amphiphilic **3T5O** molecule is accompanied with solvent effects. The **3T5O** molecule may have assumed different twisting angles, stabilized by the solvating effect of the solvent, yielding distinct absorption and emission characteristics.

**Absorption and Fluorescence Spectroscopy of 3T5O with  $\text{Ca}^{2+}$ .** For the cation detection experiment, **3T5O** was dissolved in methanol with tetrabutylammonium chloride (TBACl) as a standard. Solutions of NaCl, KCl,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$  with TBACl in methanol were used for titration with the **3T5O**

solution. There were no significant differences in the NaCl, KCl, and  $\text{MgCl}_2$  solution spectra.  $\text{Mg}^{2+}$  ions showed some weak change at  $1.6 \times 10^{-7}\text{ M}$  (Supporting Information, Figures S2 and S3). However, the predominant absorption band around 300 nm showed an increase and a blue shift when  $\text{CaCl}_2$  solution was added. A concentration of  $8 \times 10^{-8}\text{ M}$  of calcium cations was added and stirred with the  $4.8 \times 10^{-8}\text{ M}$  solution of **3T5O** (Figure 3) or 2:1 ratio. Further addition of calcium cations increased the concentration of solution up to  $12 \times 10^{-7}\text{ M}$  or 24 times the concentration of **3T5O** and the UV-vis absorption band increased linearly with increasing concentration. Thus, the primary absorption band of **3T5O** at 300 nm was increased and blue-shifted as the concentration of calcium cations increased (Figure 3a). However, the small band at 350 nm decreased and the small shoulder around 320 nm increased. This can be attributed to the phenyl ring–terthiophene dendron moieties’ increasing interaction with the calcium cation.<sup>27c</sup> The phenomenon indicates a disruption of the conjugated system in the chromophore. However, other cations, such as potassium, magnesium, and sodium did not exhibit this effect with the **3T5O** in solution (Figure 3b), e.g., when potassium and magnesium cations were added at over  $8 \times 10^{-7}\text{ M}$ , which is 20 times of the concentration of **3T5O**. Thus, no change was produced even at higher concentrations.

The fluorescence spectra showed a much more dramatic change than the UV-vis spectra. A large new band appeared when the  $\text{CaCl}_2$  solution (Figure 3c) was added to the **3T5O** solution, whereas the response to the other cations NaCl, KCl, and  $\text{MgCl}_2$  was minimal (Figure 3d). The term **3T5O3T** is now used to describe the calcium ion complex with the terthiophene dendron, **3T5O**. This new emission at 320 nm is in contrast to most fluorescence sensing systems which results in quenching or a turn-off. Thus, this system produces a “turn-on” mechanism specifically with calcium cations. The emission band at around 450 nm can be attributed to the conjugated system of terthiophene and phenyl ring as described earlier. However, the large band that appeared at 320 nm and blue-shifted relative to 450 nm after calcium cations were added can be explained with the same hypothesis presented with the UV band increase and blue-shifting; the planar  $\pi$ -conjugated system of the terthiophene dendron chromophore is twisted and disrupted. Raman spectroscopic studies would be useful in verifying the functional group responsible for the large band at 320 nm. Nevertheless, a comparison with previous studies conducted by Van Loon et al.,<sup>49</sup> Kapitan et al.,<sup>50</sup> and Feng et al.,<sup>51</sup> was done to confirm



**Figure 3.** Absorbance and emission spectra of **3T5O3T** with cations: (a) UV-vis spectrum in methanol with increasing  $\text{Ca}^{2+}$  concentration, i.e., from  $8 \times 10^{-8}$  M to  $12 \times 10^{-7}$  M ( $b = 1$  cm), (b) with increasing  $\text{Na}^+$  concentration; (c) fluorescence which was excited at 300 nm with increasing  $\text{Ca}^{2+}$  concentration and (d) with increasing  $\text{Na}^+$  concentration (emission and excitation slit widths = 10 nm).

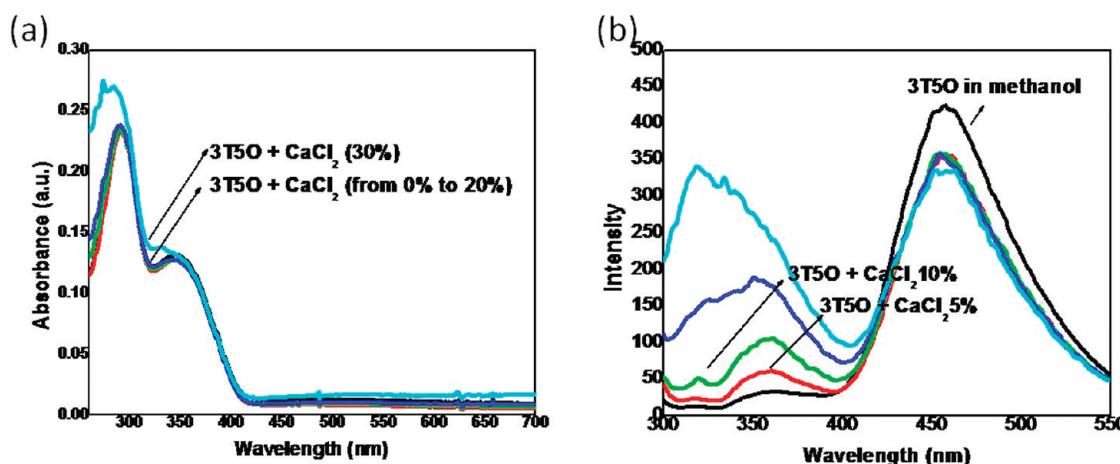
that the peak at 320 nm was not due to methanol. With reference to the Raman peak assignments, they have reported for neat methanol, aqueous salt solutions ( $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{NaCl}$ ) and powdered polyethylene glycol (PEG), respectively. Results would show that the distinct band at 320 nm, visibly seen as giving incremental changes in absorption and fluorescence intensities, pertains to that of the twisted terthiophene dendron chromophore. There is also a possibility of contribution from the hydroxyl TEG group of the **3T5O** terthiophene dendron. As reported by Tummler et al.,<sup>56</sup> solvent molecules of methanol are not too tightly bound, and hence will not strongly interfere with electrostatic interaction between the metal ion and the coordinating sites of the ligand. It is therefore presumed that methanol posed no potential interference in the determination of the absorption and fluorescence peaks for the “turn-on” sensing of calcium ions by **3T5O** terthiophene dendron.

The addition of  $\text{Na}^+$  ions upon solution of **3T5O** resulted to increasing but broad, undefined absorption and emission peaks which may be attributed to the relative weak affinity of the monovalent  $\text{Na}^+$  with ethylene glycols.<sup>52</sup> Still higher binding constants have been reported in the case of doubly charged cations such as  $\text{Ca}^{2+}$ .<sup>53</sup>

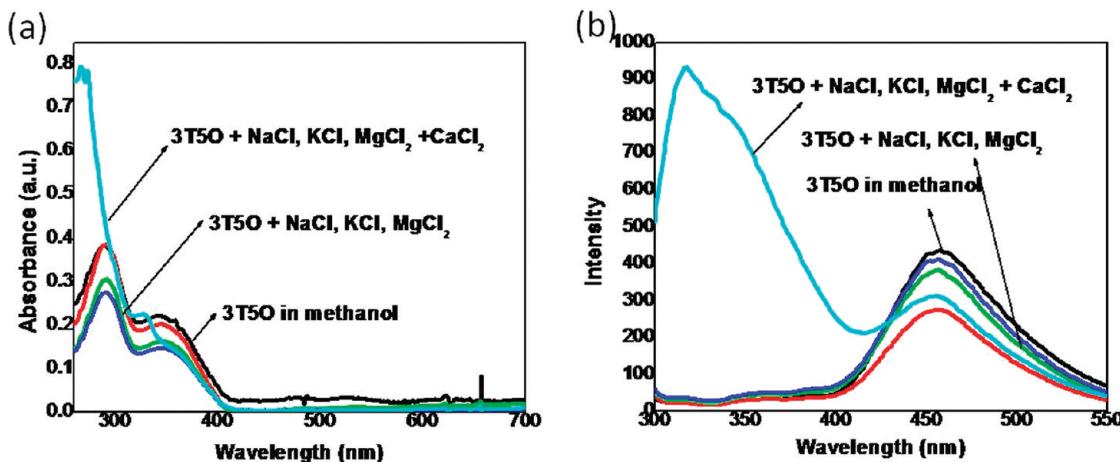
A twisted structure of the terthiophene–phenyl conjugated chromophore should explain the blue shift and intensity increases in the absorption and emission spectra using the TICT theory. Twisted thiophene molecules within the terthiophene dendron moiety form a complex with the calcium cation. This paired interaction with the calcium cation should represent a minimum energy conformation condition with a synergistic effect on enhancing fluorescence attributed to a higher energy phenyl–terthiophene excited state. Initially, the presence of a phenyl group next to the terthiophene dendrons, should conform

all the thiophenes and phenyl group to lie flat, constructing a more extended  $\pi$ -conjugated system of a particular minimum energy. However, in the presence of calcium cations interacting with the S on the thiophenes and the effect of the TEG unit complexing with the calcium ions in a crown ether effect, the molecule is conformed to a lower energy conformation that then disrupts the conjugation of the chromophore. This in turn causes the blue shift and a higher energy emission at 320 nm since the energy transfer pathway is removed from the fluorophore and replaced by a metal–ligand charge transfer (MLCT).<sup>23,24</sup> The results observed in the absorption and emission spectrum in essence are due to the twisted structure that can be more aptly explained by a TICT. It is also consistent with higher concentrations of  $\text{Ca}^{2+}$  relative to **3T5O** giving a linear plot, since more ions are made available. This will be shown by the semiempirical PM3 and Hartree–Fock calculations at the latter part of this paper. First there is a need to complete all the experimental results:

**Sensitivity Studies.** Normally, the saturation of the peaks prevents quantitative experiments for cation detection. Specifically a 1:1 matching system can only detect a 1 equiv concentration of the cationic species; i.e., no more band changes can be observed with continued addition of the analyte. However, for the **3T5O3T** system, it was shown that an incremental increase of absorbance with no saturation after addition of up to 24 equiv of the calcium cations can still be observed. This system can also detect smaller portions of the cations at  $1 \times 10^{-8}$  M. This means that this system has a high linear dynamic range compared to other solution cation sensors. Thus, the  $I/I_0$  versus  $[\text{Ca}^{2+}]/[3T5O]$  can be plotted as shown in Figure 3. A calculated slope of 1.7 indicates that the amount of calcium cations against the **3T5O** amplifies the emission peak



**Figure 4.** (a) Absorption spectra ( $b = 1\text{ cm}$ ) and (b) emission spectra with **3T5O** solution and up to 30% molar ratio of calcium cations for sensitivity (excitation and emission slit widths = 10 nm).

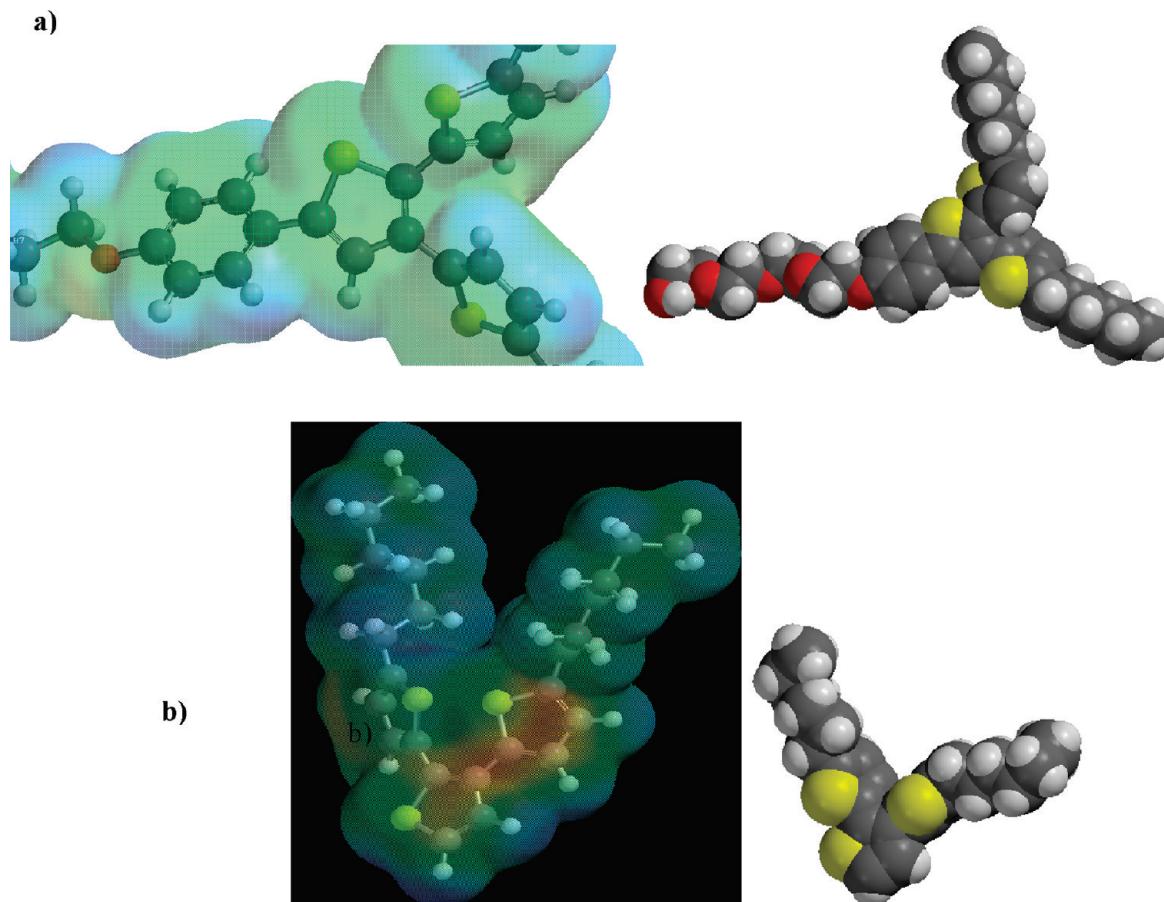


**Figure 5.** Change of the absorbance and emission when calcium cation is added to the pool of sodium, potassium and magnesium cations with compound of **3T5O**: (a) UV-vis absorption change ( $b = 1\text{ cm}$ ) and (b) emission of the solution of cations and **3T5O** (excitation and emission slit widths = 10 nm).

to be about twice the expected 1:1 correspondence in most solution sensing systems.<sup>9–12</sup> Furthermore, a solution of **3T5O** can detect calcium cations as small as 10% molar ratio (Figure 4). Since the **3T5O**T solution has more than 24 times the molar ratio of calcium cations, the UV-vis spectrum changed at a minimum of 30% molar ratio and the fluorescence changed at a minimum of 10% molar ratio. When calcium was added to the solution with 30% molar ratio, the small absorbance shoulder around 350 nm was reduced, and a separate shoulder appeared around 330 nm, while the primary band at 300 nm blue-shifted. The response in the fluorescence was more sensitive compared to the UV-vis spectra and as a result, even with 5% molar ratio of calcium cation, a band around 360 nm appeared, which was not as predominant a signal compared to the common emission band at 460 nm. However, as little as 10% of calcium cation addition produced the small peak around 320 nm. This region would eventually produce a broad emission upon addition of larger amounts of calcium cation indicating its relevance in calcium ion detection. Thus, this higher energy emission is a consequence of reduced conjugation by the twisting of the terthiophene rings in complexation with the calcium ions alone even at lower ion concentrations. Moreover, a larger dynamic range can be utilized. Semiempirical PM3 modeling studies confirm this favorable twisted conformation in the presence of the complexed calcium ion with the presence of possible cross-linking around the  $\text{Ca}^{2+}$  ions at higher **3T5O** concentration.

**Selectivity Studies.** Calcium detection was also performed with a mixture of cations present. No change was observed in the spectrum when each of the  $2.4 \times 10^{-7}\text{ M}$  sodium, potassium, and magnesium ions was added directly to the **3T5O** solution. However, the addition of calcium cations to the solution containing **3T5O** and the other three cations brought a dramatic change in UV-vis and fluorescence spectrum (Figure 5) similar to that observed with calcium ions alone. The same amount of calcium cations analogous with the other cations made the system respond strongly even at this concentration. This means that even with the presence of the other ions, both monovalent  $\text{Na}^+$  and  $\text{K}^+$  and the divalent  $\text{Mg}^{2+}$ , the molecule is strongly selective and specific for  $\text{Ca}^{2+}$ . Again, this selectivity will be confirmed by the Hartree–Fock level calculations described below.

**Molecular Modeling Studies.** The proposed fluorescent TICT mechanism for the “turn-on” sensing system for calcium ion by this terthiophene dendron with hydroxyl-terminated TEG group offers very important applications in analytical chemistry, medical analysis, and environmental monitoring.<sup>46</sup> TICT mechanism as proposed by Grabowski et al.<sup>23</sup> is anchored on observing dual fluorescence due to a twisted charge transfer state in which planarity is lost. To this end, it is only appropriate to illustrate the changes on the conformation of this terthiophene dendron upon sensing of Ca ion through modeling/computational studies using the Spartan 08 software. Computations were



**Figure 6.** Optimized geometry of the (a) **3T5O** molecule and the (b) terthiophene dendron with the space-filling model and ball and spoke model and electron (density) cloud map. The space filling model is given to ascertain the molecular size of the optimized geometry relative to each other.

performed using the semiempirical model, PM3, to obtain the equilibrium geometry at the ground state for each Ca to **3T5O** ratio. Additionally, bond angles, bond distances, stabilization energies for complexes and others as obtained from these calculations would be useful in supporting the experimental results generated from the ionoselective behavior of the terthiophene dendron toward calcium ions. The computational method was chosen to avoid extensive computing time and resources. Geometry optimizations using other models for large systems are expected to be difficult due to the increased number of basis functions as well as the increase in the degrees of freedom. Moreover, the total charge for the complex was assumed neutral since calcium atom was used to illustrate the sensing response of the **3T5O** molecule toward calcium.

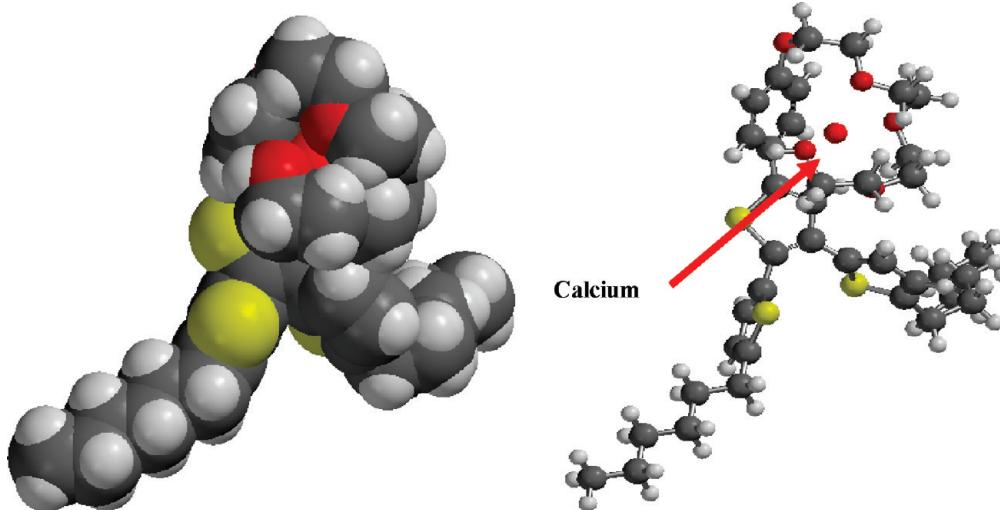
The structures shown in Figure 6 are obtained for (a) **3T5O** (emphasis was made to show the conformation of the thiophene units and the phenyl ring) and (b) a terthiophene dendron after geometry optimization using the semiempirical PM3 model (Spartan 08, wave function). It is clearly seen that the thiophene units comprising the terthiophene dendron assume a slightly twisted yet planar conformation. Sulfur atoms are denoted as S2 and S3 and are about 2.4 Å apart from each other. The bond angles formed by close association of carbon and sulfur atoms comprising the twisted thiophene units are given in Table 1. This observation corroborates earlier studies which concluded that, in the gas phase, the 2,2'-bithiophene is twisted around the 2,2'-bond and occurs in at least two conformations.<sup>31,32</sup> Previous studies have also indicated that the polythiophene configuration is affected and modified by the environment.<sup>33</sup> Direct evidence for chain flexibility in solutions obtained from

**TABLE 1: Bond Angles Observed in the Twisted Conformation of the Thiophene Units**

atoms	bond angle, deg
C10, C12, S2	122.40
C11, C12, C10	127.06
C12, C10, S1	120.59
C18, C9, C7	121.76
C17, C18, C9	125.94
C9, C18, S3	123.89

small-angle neutron scattering of undoped poly(butylthiophene) has also been previously investigated.<sup>34,35</sup> This slightly twisted conformation of the thiophene units is retained similarly in the **3T5O** molecule even with a phenyl group and ethylene glycol moieties attached to the polymer backbone. The presence of the additional phenyl chromophoric group would explain the observed blue shift as well as the increase in the intensities both in the absorption and emission maxima. Moreover, there has been indirect evidence which suggests that soluble polythiophenes modify their absorption spectra (color) from the solid to the dissolved state, and also upon melting.<sup>36</sup>

The geometry optimization performed on the 1:1  $\text{Ca}^{2+}$ /**3T5O** complex would show that there is also a significant interaction between the calcium atom and the TEG moiety of the **3T5O**. A very strong ionic bond coupled with electrostatic interactions aptly describes the interaction of the hydroxyl-terminated TEG group with calcium. The electronic configuration of alkaline earth ions such as  $\text{Ca}^{2+}$  promotes stronger ion–dipole electrostatic forces, enabling the formation of a critical ionic bond via donation of the lone *s* electron to an oxygen atom.<sup>54</sup> This



**Figure 7.** Predicted geometry of 1:1 Ca/3T5O complex with the space-filling model and ball and spoke model.

interaction is manifested through a change in the geometry of the **3T5O** molecule in the presence of the calcium atom. Without the calcium atom, the ethylene glycol units of the **3T5O**, though the repeating  $-\text{CH}_2-\text{CH}_2-\text{O}-$  group is bent but arranged in a linear fashion. However, in the presence of the calcium atom, these glycol units curled up, with the calcium atom apparently trapped beneath this conformation. The conformational flexibility of the side chain-substituted poly-thiophenes has also been observed in several studies.<sup>37–42</sup> Consequently, this phenomenon causes a shift in the absorption maxima in the visible region. Changes in the optical properties are commonly associated with the chemical and the geometrical structure of a polymer.<sup>43</sup> As shown in Figure 7, simultaneous with the encircling of calcium by the hydroxyl terminated TEG group is the enhanced by the twisting of the terthiophene dendron resulting to lost of the planar conformation which have been observed in Figure 6a. The two thiophene units have arranged themselves perpendicular to the plane of the thiophene unit that is sandwiched by these two thiophene units. This observation confirms that the terthiophene dendron has assumed a different twisting angle upon the addition of calcium ions resulting to variations on experimentally obtained absorption and emission spectra. The calcium ion induced self-assembly of the TEG group may be thought of as a major cocontributor in the peak observed at 320 nm shown in the emission spectrum. This band at 320 nm further affirms the strongly polar character and relative mobility of the TEG hydroxyl segment of the terthiophene dendron, enhancing the signaling response in the presence of calcium ions. Moreover, it has been clearly demonstrated in Figure 7 that the enhancement in the absorption and emission peak is due to the less stretched conformation of the terthiophene dendron resulting in a lower hydrodynamic volume similar to coil-like polymers brought about by the coiling of the hydrophilic TEG side chain, dictating the “turn on” mode for the sensing of calcium ions. Differences in the energy are normally found and in the case of sensing of calcium by the **3T5O** molecule, the average calculated energy (heat of formation) of an optimized 1:1  $\text{Ca}^{2+}/\text{3T5O}$  complex is  $-1457.46 \text{ kJ/mol}$ .

Calculations were also performed for the 1:2 and 1:4  $\text{Ca}/\text{3T5O}$  systems using the semiempirical model (PM3). Results suggest that in the presence of additional **3T5O** units (or at smaller concentration of the ions), a cage-like structure is formed due to possible cross-linking or aggregation arising from chromophore–chromophore interactions such as the hydroxyl

**TABLE 2: Calculated Distances between Calcium Atom and the Oxygen Atoms of 3T5O, 1:4 Ca to 3T5O Molar Ratio**

labels	distance, Å
O3, Ca1	2.668
O17, Ca1	2.760
O2, Ca1	2.491
O15, Ca1	2.498
O19, Ca1	2.590
O20, Ca1	2.496
O18, Ca1	2.532

TEG group of the dendron, dendron–dendron dimerization, or solvent–dendron interactions. Cross-linking arises due to the interplay of electrostatic interactions, hydrogen bonding, and van der Waals interactions among different components present in solution. It is ascertained that the calcium atom is somewhat encapsulated during the cross-linking process by the TEG groups and likewise the terthiophene units by a favorable  $\pi-\pi$  stacking. Table 2 gives the calculated distances between the calcium atom and the oxygen atoms with 4 units of **3T5O** molecule.

The calculated heat of formation for the 1:4  $\text{Ca}/\text{3T5O}$  complex is  $-3779.88 \text{ kJ/mol}$  and that for the 4 units of **3T5O** only (without calcium) is around  $-2463.89 \text{ kJ/mol}$  which accounts for the **3T5O/3T5O** self-interactions. Using the equation below, the stabilization energy for the complex is determined to be  $-1494.23 \text{ kJ/mol}$ .

$$\Delta E = E_{\text{Ca/3T5O complex}} - [E_{\text{Ca/3T5O}} + E_{\text{Ca}}] \quad (1)$$

In the determination of the energy differences for this particular system, the procedure employed by Cece et al.<sup>44</sup> in treating their calculated data can fully explain the interaction of ethane and hexafluoroethane with carbon dioxide. Table 3 summarizes the calculated energies for the different  $\text{Ca}/\text{3T5O}$  complex systems. The first column of values is the energy (heat of formation) of the optimized geometry of the complex formed by the interaction of calcium with varying numbers of **3T5O** units. On the other hand, the second column contains the sum of the energies of the individual components which make up the complex:  $\sum E(\text{heat of formation}) = \sum E(\text{3T5O units}) + E(\text{calcium atom})$ . The third column gives the single-point energy of the **3T5O** units calculated at different ratios while the fourth column shows the energy of the calcium atom extracted from the optimized geometries for each  $\text{Ca:3T5O}$  molar ratio. The

**TABLE 3: Energies (kJ/mol) of Ca/3T5O Interactions<sup>a</sup>**

Ca to <b>3T5O</b>	heat of molar ratio, formtn of complex	$\Sigma E$ of components	single-point calcns of heat of formn of <b>3T5O</b>	$\Delta E$ of Ca from complex (varying ratios)
1:1	-1457.4624	-401.462	-579.70	178.238
1:2	-2470.524	-981.162	-1202.695	221.533
1:4	-3779.88	-2140.562	-2463.889	323.327

<sup>a</sup> Heat of formation of an isolated Ca atom = 178.238 kJ/mol; heat of formation of an isolated **3T5O** unit = -579.70 kJ/mol.

tabulated results imply that the presence of varying molar amounts of **3T5O** may have induced changes upon the calcium atom. The change in the energy (heat of formation) of calcium extracted from the complex was found to have deviated from the single-point calculation performed for calcium atom alone. As the amount of **3T5O** unit was increased, the change in energy for calcium from the complex has been noted to increase. Interestingly, the data shown in Table 3 validates that the sensing of calcium ions by the terthiophene dendron having a hydroxyl-terminated TEG chain is accompanied by changes in the enthalphy of ligand complexation arising from a number of factors which include intermolecular **3T5O**-**3T5O** interactions (as also shown in Table 4),  $\pi-\pi$  stacking of the phenyl ring attached to the TEG side chain of the terthiophene dendron and the steric deformation brought about by the coiling of calcium by the TEG group. Also, results of the calculations carried out for each molar ratio of Ca to **3T5O** suggests that a single **3T5O** dendron unit provides better stabilization for the calcium ion ( $\Delta E = 178.238$  kJ/mol) during the complexation reaction, resulting in an efficient sensing of calcium ions. More so, the relative polarizability of the dendron has been established, thus realizing the desired conformational change on the dendron as induced by the calcium ion, which is a pivotal requirement in the occurrence of TICT phenomenon.

The first column in Table 4 gives the difference between the energy of the optimized geometry of the complex formed by the interaction of **3T5O** with calcium and the summation of the energies of the individual components which make up the complex. The difference between the values obtained from single-point energy calculations of varying **3T5O** units (energy of the cluster of **3T5O** molecules in the complex) and the sum of the energies of individual **3T5O** units (-579.70 kJ/mol) represents the energy of interaction of the **3T5O** units with one another is given in the second column. The last column indicates the interaction energy between the **3T5O** molecule and the Ca atom in the system. This value is the difference between column 1 and column 2 of Table 4.

Thus, the data given in Table 4 provides for the calculated change in the energy for systems with varying molar ratios of Ca/**3T5O**. The change in the energy accounts for the changes in the geometry of the **3T5O** as it accommodates/interacts with the calcium atom. Consequently, this change in geometry would explain the observed sensing of calcium by the **3T5O** molecule and with increasing ratio; it gives unfavorable interaction primarily due to cross-linking or “aggregating” around the ion by the TEG group. Also, the calculated change in the energy upon interaction of a **3T5O** unit with calcium ion ( $\Delta E = 1056.004$  kJ/mol) is more significant compared with the change in the energy for the **3T5O**/**3T5O** interactions, particularly in the case of 1:1 molar ratio, which is marked by the absence of dendron-dendron interaction ( $\Delta E_{3T5O/3T5O} = 0$  kJ/mol).

In an effort to distinguish specific interactions between monovalent and divalent cations and **3T5O**, calculations at

**TABLE 4: Interaction Energies for Ca/3T5O Systems (kJ/mol)**

no. of 3T5O units	total energy of interaction between Ca and 3T5O	energy of interaction of 3T5O with one another	interaction energy between the 3T5O molecule and the Ca atom in the system
1	-1056.0004	0.0	-1056.0004
2	-1489.362	-43.295	-1446.067
4	-1639.318	-145.089	-1494.229

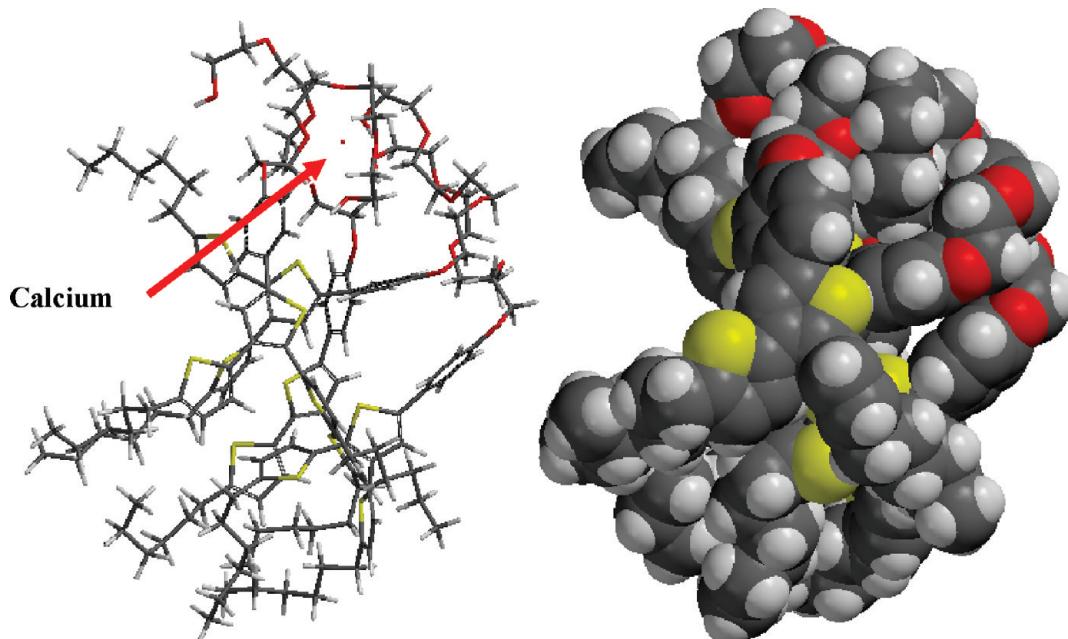
**TABLE 5: Calculated Stabilization Energies for 1:1 Cation/3T5O Complex System (kJ/mol)<sup>a</sup>**

cation	energy of the complex	energy of the cation	stabilzn energy, $\Delta E$
Ca <sup>2+</sup>	-3670.4347	-669.4335	-0.4483
Mg <sup>2+</sup>	-3197.4895	-196.5119	-0.4247
K <sup>+</sup>	-3593.6728	-593.0093	-0.0711
Na <sup>+</sup>	-3160.395	-159.7846	-0.0626

<sup>a</sup> Energy of single **3T5O** molecule = -3000.552 826 kJ/mol.

the restricted Hartree-Fock level theory using the STO-3G basis set were performed. The semiempirical model (PM3) is not parametrized for calculations involving sodium and potassium ions. The charge of the cation is taken as the total charge for each complex/system. Single-point calculations were also performed at the STO-3G level on varying ratios of **3T5O** units and on separate cations to determine if any of the observed energy differences were due to **3T5O**/**3T5O** interactions. Calculations were carried out with the assumption that the solvent-induced changes for the formation of complexes are negligible; i.e., concentrations of the solutions used in generating the experimental data were not very diluted to make the system/complex highly solvated to cause significant changes. The values shown are average of three calculations per complex/system.

Results of these calculations as summarized in Table 5 show that, between monovalent and divalent ions, the divalent ions such as calcium and magnesium provide a more stable complex with the **3T5O** unit over the monovalent species such as potassium and sodium cations. Moreover, it is the calcium dication which gives a relatively more stable complex with **3T5O** with net stabilization energy equal to -0.4483 kJ/mol compared with magnesium, which may be used to explain for the observed preferential sensing of calcium ions by the terthiophene dendron in the presence of the other three cations used for the selectivity experiments. The stabilization energy calculated further validates the ability of the TEG group to optimally bind with the Ca<sup>2+</sup> ions. Optimal binding may then be correlated with maximized interactions within the cavity/cage that is formed from the encircling of the hydroxyl-terminated TEG group in the presence of a Ca<sup>2+</sup> ion. The size of the cage/cavity thus created from the curling of the TEG group is commensurate to that of the size of the Ca<sup>2+</sup> ion and, accordingly, may be regarded as the most favorable conformation for the desired TICT “turn on” sensing of calcium ion by the **3T5O** dendron. Similarly, cyclic receptors such crown ethers demonstrate the same behavior toward cation binding, termed as hole-size relationship.<sup>54</sup> Moreover, calculated data presented in Table 5 further support the experimental data obtained from sensing of Na<sup>+</sup> ions by terthiophene dendron **3T5O**. It has been previously discussed that the weak affinity of the monovalent cations such as Na<sup>+</sup> to ethylene glycol resulted to broadened, undefined increments on the emission intensity upon addition of increasing concentrations of Na<sup>+</sup> ions. This could be due



**Figure 8.** Predicted geometry for the 1:4 Ca/3T5O mole ratio as illustrated using the ball and stick (left) and space-filling models (right).

to the weak electrostatic forces existing between the TEG group and the  $\text{Na}^+$  ion. Such weak affinity can be ascribed to the inert  $\text{np}^6$  electronic configuration of  $\text{Na}^+$ .<sup>54</sup>

In summary, the findings in this work have yet to realize practical sensor applications. But the molecular/macromolecular design properties have been laid out for any future synthesis. As discussed, the possibility of using a “turn-on” system has many advantages over “turn-off” systems.

## Conclusion

We have reported on a designed  $\text{Ca}^{2+}$  ion sensing molecule consisting of a branched or dendronic terthiophene with tetraethylene glycol moiety (**3T5O**). The sulfur atoms of the terthiophene dendron moiety contribute to the metal–ligand complexation of calcium cations, the presence of the hydroxyl-terminated TEG group enabling a TICT event to occur in the presence of the  $\text{Ca}^{2+}$  analyte. This resulted in distinct emission intensity (320 nm) at the same time producing a blue shift in the absorption which enabled a “turn-on” system for calcium ion detection. A high sensitivity up to  $1 \times 10^{-8}$  M for calcium and a high selectivity against  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  was observed. These observations were confirmed by a conformational analysis of the (**3T5O**) and the twisted terthiophene dendron geometry using semiempirical PM3 modeling and restricted Hartree–Fock level calculations using the STO-3G basis set. Possible experiments in the future would be comparison with other buffered physiological conditions including blood plasma.

**Acknowledgment.** The authors gratefully acknowledge funding from the National Science Foundation DMR-10-06776, CBET-0854979, and Robert A. Welch Foundation, E-1551. D.C.A. acknowledges support from DOST-PCAST-TRD Philippines.

**Supporting Information Available:** Experimental details of synthesis, characterization, and absorbance and emission spectrum of other cations are reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) (a) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, 197. (b) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, 97, 1515. (c) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, 205, 3. (d) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, 100, 2537. (e) Wiskur, S. L.; Ait-Haddou, H.; Lavigne, J. J.; Anslyn, E. V. *Acc. Chem. Res.* **2001**, 34, 963. (f) Gokel, G. W.; Leevy, W. M.; Weber, M. E. *Chem. Rev.* **2004**, 104, 2723.
- (2) Arunkumar, E.; Ajayaghosh, A.; Daub, J. *J. Am. Chem. Soc.* **2005**, 127, 3156.
- (3) Arunkumar, E.; Chithra, P.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2004**, 126, 6590.
- (4) (a) Morozumi, T.; Hiraga, H.; Nakamura, H. *Chem. Lett.* **2003**, 32, 146. (b) Kakizawa, Y.; Akita, T.; Nakamura, H. *Chem. Lett.* **1993**, 1671.
- (5) Kokubo, K.; Kitasaka, K.; Oshima, T. *Org. Lett.* **2006**, 8, 1597.
- (6) Prodi, L.; Bargossi, C.; Montalti, M.; Zaccheroni, N.; Su, N.; Bradshaw, J.; Izatt, R.; Savage, P. *J. Am. Chem. Soc.* **2000**, 122, 6769.
- (7) Prodi, L.; Bolletta, F.; Zaccheroni, N.; Watt, C. I. F.; Mooney, N. *Chem.—Eur. J.* **1998**, 4, 1090.
- (8) Grandini, P.; Mancin, F.; Tecilla, P.; Scrimin, P.; Tonellato, U. *Angew. Chem., Int. Ed.* **1999**, 38, 3061.
- (9) Gokel, G. W. *Crown Ethers and Cryptands*; Royal Society of Chemistry: London, 1991.
- (10) Hiraoka, M. *Crown Ethers and Analogous Compounds*; Elsevier: New York, 1992.
- (11) Takagi, M.; Ueno, K. *Host Guest Complex Chemistry*; Springer: Berlin, 1984.
- (12) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1978.
- (13) D’Souza, V. T.; Lipokwitz, K. B. *Chem. Rev.* **1998**, 98, 1741.
- (14) Shinkai, S. *Tetrahedron* **1993**, 49, 8933.
- (15) Shinkai, S. *Advances in Supramolecular Chemistry*; JAI Press: Greenwich, CT, 1993; Vol. 3.
- (16) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: London, 1989.
- (17) Miyoshi, D.; Karimata, H.; Wang, Z.; Koumoto, K.; Sugimoto, N. *J. Am. Chem. Soc.* **2007**, 129, 5919.
- (18) Nabeshima, T.; Yoshihira, Y.; Saiki, T.; Akine, S.; Horn, E. *J. Am. Chem. Soc.* **2003**, 125, 28.
- (19) (a) Bryan, A. J.; de Silva, A. P.; de Silva, S. A.; Rupasinghe, R. A. D. D.; Sandanayake, K. R. A. S. *Biosensors* **1989**, 4, 169. (b) de Silva, A. P.; Gunaratne, H. Q. N. *J. Chem. Soc., Chem. Commun.* **1990**, 186. (c) de Silva, A. P.; Gunaratne, H. Q. N.; Maguire, G. E. M. *J. J. Chem. Soc., Chem. Commun.* **1994**, 1213. (d) de Silva, A. P.; Gunaratne, H. Q. N.; Kane, A. T. M.; Maguire, G. E. M. *J. Chem. Lett.* **1995**, 125.
- (20) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C. *Org. Lett.* **2002**, 4, 2067.

- (21) (a) Kim, J.; Morozumi, T.; Nakamura, H. *Org. Lett. ASAP*. (b) Hama, H.; Morozumi, T.; Nakamura, H. *Tetrahedron Lett.* **2007**, *48*, 1859. (c) Morozumi, T.; Anada, T.; Nakamura, H. *J. Phys. Chem. B* **2001**, *105*, 2923.
- (22) Rotkiewicz, K.; Grellmann, K. H.; Grabowski, Z. G. *Chem. Phys. Lett.* **1973**, *19*, 315.
- (23) Grabowski, Z. G.; Rotkiewicz, K.; Siemianczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.
- (24) Rettig, W. *Top. Curr. Chem.* **1994**, *169*, 253.
- (25) Coskun, A.; Akkaya, E. *J. Am. Chem. Soc.* **2006**, *128*, 14474.
- (26) (a) Beck, J. B. B.; Rowan, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 13922. (b) Weng, W.; Beck, J. B. B.; Jamieson, A. M.; Rowan, S. J. *J. Am. Chem. Soc.* **2006**, *128*, 11663. (c) Knapton, D.; Iyer, P. K.; Rowan, S. J.; Weder, C. *Macromolecules* **2006**, *39*, 4069. (d) Zhao, Y.; Beck, J. B.; Rowan, S. J.; Jamieson, A. M. *Macromolecules* **2004**, *37*, 3529.
- (27) (a) Deng, S.; Locklin, J.; Patton, D.; Baba, A.; Advincula, R. C. *J. Am. Chem. Soc.* **2005**, *127*, 1744. (b) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C. *Org. Lett.* **2002**, *4*, 2067. (c) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C.; Gies, A.; Nonidez, W. *J. Am. Chem. Soc.* **2004**, *126*, 8735.
- (28) Taranekar, P.; Fulghum, T.; Baba, A.; Patton, D.; Advincula, R. *Langmuir* **2007**, *23*, 908.
- (29) Leclère, P.; Surin, M.; Viville, P.; Lazzaroni, R.; Kilbinger, A.; Henze, O.; Feast, W.; Cavallini, M.; Biscarini, F.; Schenning, A.; Meijer, E. *Chem. Mater.* **2004**, *16*, 4452.
- (30) Xia, C.; Locklin, J.; Youk, J.; Fulghum, T.; Advincula, R. *Langmuir* **2001**, *18*, 955.
- (31) Almenningern, A.; Bastiansen, O.; Svendsen, P. *Acta Chem. Scand.* **1958**, *12*, 1671.
- (32) Samdal, A.; Samuelsen, E.; Volden, H. *Synth. Met.* **1993**, *59*, 259.
- (33) Samuelsen, L. Mardalen, J. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley and Sons: London, 1997; Vol. 3, Chapter 2, pp 88–120.
- (34) Aime, J.; Bargain, F.; Schott, M.; Eckhardt, H.; Miller, G.; Elsenbaumer, R. *Phys. Rev. Lett.* **1989**, *62*.
- (35) Aime, J.; Bargain, F.; Schott, M.; Eckhardt, H.; Miller, G. G.; Elsenbaumer, R. L.; McDonnel, M.; Zero, K. *Synth. Met.* **1989**, *28*, C407.
- (36) Hotta, S. *Synth. Met.* **1987**, *22*, 103.
- (37) Jen, K.; Miller, G.; Elsenbaumer, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
- (38) Sugimoto, R.; Takeda, S.; Gu, H.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.
- (39) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.
- (40) Kaeriyama, K.; Sato, M.; Tanaka, S. *Synth. Met.* **1987**, *18*, 233.
- (41) Osterholm, J.; Laakso, J.; Nyholm, P.; Isotalo, H.; Stubb, H.; Inganas, O.; Salaneck, W. *Synth. Met.* **1989**, *28*, C435.
- (42) Bryce, M.; Chissel, A.; Kathigamanathan, P.; Parker, D.; Smith, N. *J. Chem. Soc. Chem. Commun.* **1987**, 466.
- (43) Inganas, O. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley and Sons: London, 1997; Vol. 3, Chapter 2, pp 785–793.
- (44) Cece, A.; Jureller, S.; Kerschner, J.; Moschner, K. *J. Phys. Chem.* **1996**, *100*, 7435.
- (45) Frampton, M. J.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 1028.
- (46) Bajorek, A.; Paczkowski, J. *Macromolecules* **1998**, *31*, 86.
- (47) De Boer, B.; van Hutton, P. F.; Ouali, L.; Grayer, V.; Hadzioannou, G. *Macromolecules* **2002**, *35*, 6883.
- (48) Grabowski, Z. R.; Rotkiewicz, K. *Chem. Rev.* **2003**, *103*, 3899.
- (49) Van Loon, L. L.; Allen, H. C. *J. Phys. Chem. B* **2004**, *108*, 17666. The Raman spectrum for neat methanol includes the following peaks: symmetric O—C stretch at 1034 and 2835  $\text{cm}^{-1}$  for the  $\text{CH}_3$  symmetric stretch and peaks arising from two Fermi resonances, 2920 and 2944  $\text{cm}^{-1}$ .
- (50) Kapitan, J.; et al. *J. Phys. Chem. B* **2010**, *114*, 3574. Experimental Raman peak frequencies of various aqueous salt solutions of  $\text{CaCl}_2$ ,  $\text{NaCl}$ , and  $\text{MgCl}_2$  (5 mol/kg, 20 °C) would show  $\delta(\text{HOH})$  and  $\nu(\text{H}\cdots\text{O}) + \delta(\text{HOH})$  peaks found at 1647 and 2060  $\text{cm}^{-1}$ , 1649 and 2063  $\text{cm}^{-1}$ , and 1651 and 2052  $\text{cm}^{-1}$  regions, respectively.
- (51) Feng, Z. V.; Li, X.; Gewirth, A. A. *J. Phys. Chem. B* **2003**, *107*, 9415. Normal Raman spectrum has been obtained for polyethylene glycol. Important peaks that may be associated with the hydroxyl-terminated TEG group of the **3T5O** terthiophene dendron are the following: 277, 361, 534, 845, and 857  $\text{cm}^{-1}$  which have been assigned to  $\delta(\text{OCC})$ ,  $\delta(\text{COC})$ ,  $\delta(\text{OCC})$ ,  $r(\text{CH}_2)$ , and  $\nu(\text{CO})$ , respectively.
- (52) Izatt, R. M.; Eatough, D. J.; Christensen, J. J. *Struct. Bonding (Berlin)* **1973**, *16*, 161.
- (53) Balbo-Block, M. A.; Hecht, S. *Macromolecules* **2004**, *37*, 4761.
- (54) Wu, H.-F.; Brodbelt, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 6418.
- (55) Hu, R.; Lager, E.; Aguilar, A. A.; et al. *J. Phys. Chem. C* **2009**, *113*, 15845.
- (56) Tummler, B.; Maass, G.; Vogtle, F.; et al. *J. Am. Chem. Soc.* **1979**, *101*, 2588.

JP1068522