Tetrahedron Letters 51 (2010) 4666–4669

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Controlled emission enhancement and quenching by self-assembly of low molecular weight thiophene derivatives

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ARTICLE INFO

Article history:
Received 10 May 2010
Revised 27 June 2010
Accepted 1 July 2010

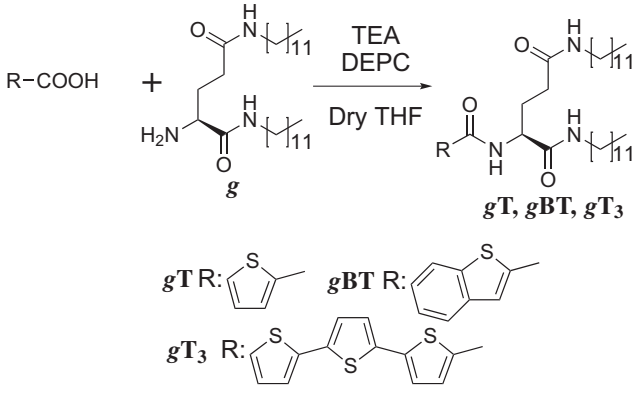
ABSTRACT

Three thiophene-containing compounds were newly synthesized as low molecular weight blocks to construct non-covalent and highly ordered π-conjugation systems. Typical emission enhancement and quenching based on the *J*- and *H*-type orientations, respectively, of the thiophene moiety were realized and controlled by lipid membrane-like phase transition and separation behaviours.

π-Conjugated molecules such as polythiophene have attracted considerable attention for their potential as alternatives to inorganic semiconductors with many advantages over existing materials, including mechanical flexibility, processability and lightweight solutions.[1] However, it is common knowledge that the low solubility and miscibility of unmodified polythiophenes[2] are major limitations in a precisely controlled fabrication, especially at the nano level. To overcome this, many chemical modifications have been developed, for example, polyalkylthiophene,[1] poly(3,4-alkylenedioxythiophene),[3] conjugated oligomer-pendant polymer[4] and so on.[5] Another solution is to adopt self-assembling low molecular weight derivatives containing a thiophene moiety. In this approach, a long-range π-conjugation would be realized by molecular ordering of the thiophene moieties; good examples are thiophene derivatives[6] modified by alkoxy, alkylureido and cholesteryl groups. Furthermore, Park et al.[7] modified this system by developing new kinds of the thiophene-containing self-assembling compounds such as 2,3-bis[5-(trifluoro-methylphenyl)thiophen-2-yl]acrylonitrile, which have neither steroidal nor long alkyl chain groups as an electro-inactive moiety and can exhibit *J*-type aggregation leading to a strong fluorescence emission on nano-crystallization.

Herein we introduce a new class of low molecular weight thiophene derivatives (***g*T**, ***g*BT,** and **gT_3**) that exhibit emission enhancement and control through lipid membrane-like functions. The molecules are characterized by the fact that they include simple thiophene structures that facilitate chemical tuning and an L-glutamide moiety that promotes and controls the molecular ordering with lipid membrane-like properties[8] such as phase transition and separation behaviours. We report herein that the designed thiophene-containing derivatives yield well-developed one-dimensional aggregates with nano-size diameters in various media, but these aggregates are not crystals and exhibit strong fluorescence emission enhancement and quenching. In addition, emission control and switching can be achieved not only by chemical tuning around the thiophene moiety but also by a thermotropically and lyotropically induced phase transition and separation behaviours.

Two kinds of the monothiophene-containing compounds (***g*T** and ***g*BT**) and one terthiophene-containing compound (**gT_3**) were newly synthesized (Scheme 1). All the compounds were functionalized by the didodecyl L-glutamide (***g***) unit which is known



Scheme 1.

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doi:10.1016/j.tetlet.2010.07.006

Table 1
Minimum gelation concentrations of thiophene derivatives at 10 °C

Solvent	**gT**	**gBT**	**gT$_3$**
n-Hexane	1 mM	1 mM	I
Methylcyclohexane	1 mM	1 mM	1 mM
Cyclohexane	1 mM	1 mM	1 mM
Toluene	30 mM	3 mM	1 mM
Benzene	30 mM	1 mM	3 mM
Chloroform	S	S	S
Ethyl acetate	30 mM	3 mM	1 mM
Tetrahydrofurane	S	S	S
Dichloromethane	S	S	S
Acetone	S	S	I
Ethanol	S	S	I
Methanol	S	S	I
Acetonitrile	I	I	I

S: soluble, I: insoluble in 1.0 mM.

as a versatile self-assembling tool for the creation of nano-sized fibrillar aggregates both in aqueous[9,10] and in non-aqueous[11–13] systems. Table S1 summarizes the dispersity (solubility) of these compounds in various organic media from methanol to *n*-hexane. Clearly, ***g*T** and ***g*BT** show good dispersity in all the solvents used in this work whereas ***g*T$_3$** shows relatively poor dispersity especially in polar alcohols and non-polar *n*-hexane. This is a further proof that monothiophene derivatives have better processability (directly related to solubility) than polythiophene derivatives.

On the other hand, mass gelation behaviours were observed by adjusting temperature and concentration in certain solvents. Table 1 summarizes apparent minimum gelation concentrations (mgc) in various solvents at 10 °C. For example, the mgc is ~1 mM in methylcyclohexane (MCH), cyclohexane and *n*-hexane at 10 °C. Mass gelation was also observed in other solvents such as benzene, toluene and ethyl acetate at a higher concentration: the mgc in benzene is 3 mM in ***g*BT** at 10 °C. Such a thermotropically and lyotropically induced gelation resembles the low molecular mass gelation through nano-fibrillar aggregation from cholesteryl, sugar-containing and peptide derivatives.[14] In fact, TEM indicated that fibrillar aggregates were produced in our thiophene derivatives: the ***g*BT** MCH solution (0.25 mM) shows well-developed fibrils with 20–30 nm diameters (Supplementary data) showing that the gelation was brought about by the formation of a three-dimensional network from the one-dimensional fibrils. Similar fibril formations were observed with ***g*T** and ***g*T$_3$** as well (Supplementary data).

The special properties of ***g*BT** and ***g*T$_3$** were furthermore emphasized in the fluorescence study. As shown in Figures 1 and 2 remarkable enhancement of the fluorescence intensity was observed with a slight red shift in the absorption spectrum

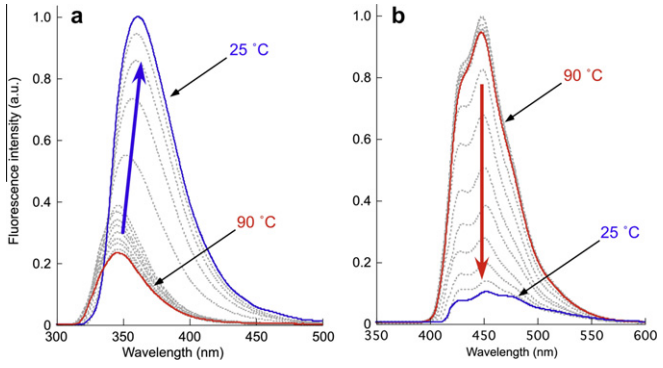

Figure 1. Temperature dependencies of fluorescence emission spectra of (a) **gBT** and (b) **gT$_3$** in MCH. [**gBT**] = 0.25 mM, [**gT$_3$**] = 0.10 mM. Excitation wavelengths: (a) 320 nm and (b) 410 nm.

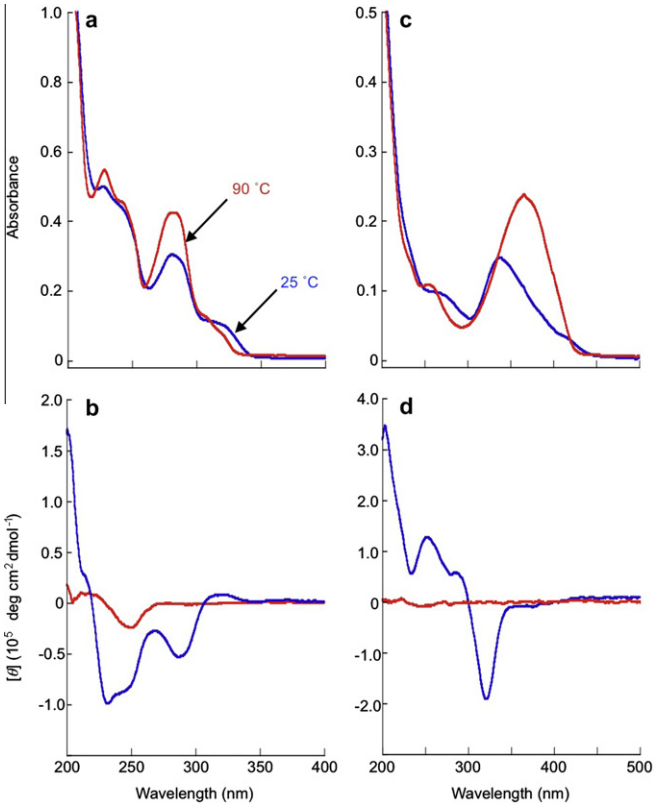

Figure 2. Temperature dependencies of UV–vis and CD spectra of (a and b) **gBT** and (c and d) **gT$_3$** in MCH. [**gBT**] = 0.25 mM, [**gT$_3$**] = 0.10 mM. Red lines, 90 °C and blue lines, 25 °C.

in a **gBT** MCH solution on changing the temperature from 90 to 25 °C, while **gT$_3$** showed remarkable fluorescence quenching. Similar fluorescence enhancement phenomenon has been called aggregation-induced emission enhancement (AIEE),[14] and the typical examples are seen in solvent-dependent crystallization of non-planar and long range π-conjugated molecules such as hexaphenylsiloles, poly(phenylene-ethynylene)s and bis(3,5-ditrifluoromethyl-phenyl)cyano-stilbene.[7,16] The fluorescence quenching is called aggregation-caused quenching (ACQ),[15,17] and it is rather common in planar π-conjugated molecules such as pyrene. However, it should be noted that there are some distinct differences between our fluorescence enhancement system and the previous AIEEs. Firstly, the chromophoric moiety of **gBT** is benzothiophene which is much smaller than the previous AIEE π-conjugated molecules. Secondly, our chromophore is planar and promotes plane-to-plane stacking, whereas AIEE is achieved by moderation of intramolecular torsional structure[16] and suppression of intramolecular vibration/torsional motions[18] by aggregation. Thirdly, **gBT** exhibits emission enhancement even at a higher concentration than 0.025 mM, which is a minimum assembly concentration (mac) at **gBT** in MCH (Supplementary data). Finally, this emission enhancement is induced thermotropically in **gBT**. The origin of these differences can be probably explained by the molecular ordering assisted with the ***g*** moiety, whereas the previous AIEE was related to the specific structure of the chromophoric groups.

We obtained several results that elucidate the mechanism of the emission enhancement in **gBT**: a **gBT** solution showed a temperature-dependent red shift on absorption of a benzothiophene moiety in UV spectroscopy. This spectral change was accompanied by a specific chirality induction. As shown in Figure 2, there is almost no CD signal at 90 °C although one exception is seen at

around 250 nm. New cotton effects appear with decreasing temperature at around 230, 285, and 320 nm which correspond to those observed in UV spectroscopy. The $[\theta]_\lambda$ values reach −9.6, −5.2, and 1.0×10^4 deg cm^2 dmol^{-1} at 230, 285, and 320 nm, respectively. Since the benzothiophene moiety has no chiral structure and almost no CD signals were detected in a good solvent such as chloroform promoting disaggregation, the specific chiroptical behaviours are assigned to an induction of secondary chirality such as chiral π–π stacking with a *J*-type (head-to-tail) orientation[10,11] among the thiophene moieties (Fig. 3). In addition, neither a red shift nor an induction of CD was observed in benzothiophene without the ***g*** moiety, and thus these specific chiral arrangements must be promoted by chirally self-assembling property of the ***g*** moiety.

By contrast, gT_3 showed a blue shift with an induced CD (Fig. 2) indicating a *H*-type (head-to-head) orientation[11–13] and **gT** showed no significant spectral changes under the same condition. Interestingly, all the thiophene derivatives (**gT**, **gBT**, and **gT$_3$**) can form nano-sized fibrillar aggregates at 0.10–0.25 mM in MCH. These results suggest that their critical aggregation concentrations are much lower than their mgc and their stacking structures are remarkably tuned by the chemical structures around the thiophene moieties. Furthermore, it is presumable that an asymmetric structural thiophene such as **BT** tends to exhibit *J*-type stacking[19], whereas a symmetric structural thiophene such as **T$_3$** tends to exhibit *H*-type stacking (Fig. 3). On the basis of these assumptions, **gT** must be similar to **gT$_3$** but the thiophene–thiophene interaction may be too weak to allow the detection of the stacked structure by UV and CD spectroscopy.

On the basis of these results, we conclude that the emission enhancement and quenching with the ***g*** derivatives are closely related to *J*- and *H*-type orientations among the thiophene moieties, respectively. In addition to the above, we found that emission control could be achieved by phase separation phenomenon[12,20] in a binary component system. The successful example was obtained as follows: a β-aminopropanoyl L-glutamide derivative (**gAP**)[10] was selected as the matrix component because of its good solubility in a wide range of solvents (from water to *n*-hexane) as well as its high self-assembling ability in these media. A mixed system composed of **gBT**–**gAP** (1:5) was prepared by dissolution in hot MCH. At 90 °C, the fluorescence intensity was very similar to that observed in a system with **gBT** alone. There was no significant CD induction in the absorption band around the thiophene moiety. Therefore, it is estimated that **gBT** is in monomeric or disordered states at 90 °C regardless of **gAP**. On the other hand, the fluorescence intensity increased when the temperature was reduced (Fig. 4a): example 1.3- and 1.7-fold at 25 and −5 °C, respectively. Further increase (3.8-fold) was observed by the addition of a small amount (1.0 equiv) of sulfuric acid. According to the concentration dependency of sulfuric acid on the fluorescence intensity (Fig. 4b),

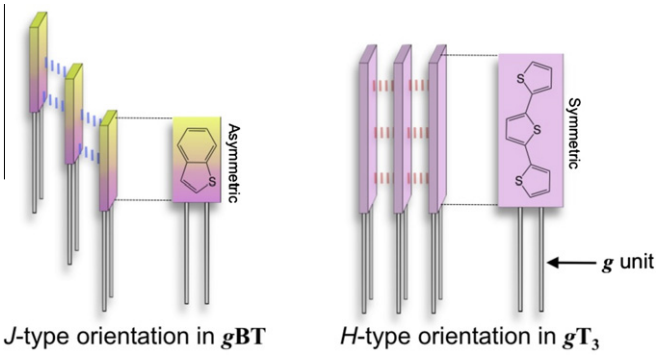

Figure 3. *J*- and *H*-type orientations promote emission enhancement and quenching, respectively.

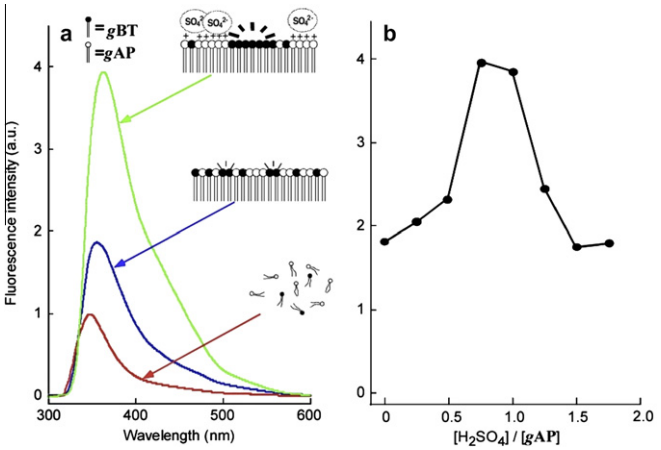

Figure 4. (a) Fluorescence emission spectra of the **gBT**–**gAP** (1:5) mixed system in MCH at 90 °C (red), −5 °C (blue), and −5 °C with 1.0 equiv of sulfuric acid (green). (b) Concentration dependency of sulfuric acid on the fluorescence enhancement at 365 nm at −5 °C. **gAP**: ***g***–$(CH_2)_2$–NH.

the critical enhancement occurs in the range of 0.75–1.0 equiv of sulfuric acid against **gAP**. Additionally it was confirmed that the UV and CD spectra approached those in a system with **gBT** alone. These results indicate that the binary component system provides a phase separation phenomenon[12,20] that allows creation of **gBT** domains in the **gAP** matrix which can be promoted by not only temperature decrease but also electrostatic interaction with sulfuric acid as an external stimulus. Figure. 4a includes a schematic illustration of the phase separation-induced emission enhancement. Such a similarity to lipid membrane functions is clearly based on the characteristics of the lipid-like ***g*** moiety.

In conclusion, we have established controlled aggregation-induced emission enhancement and quenching in a new class of low molecular weight thiophene derivatives. The solubility was considerably improved by derivatization of monothiophene, and an intramolecular π-conjugation was realized through controlling the molecular ordering states, viz., the *J*- and *H*-type orientations of the thiophene moiety. In addition, we realized emission control by using the phase separation behaviour in a binary component system. This success is due to using a lipid-like self-assembling unit, and therefore, may have possible applications in molecular switching devices.

Experimental

Synthesis of *N*,*N*′-didodecyl-*N*′-(2-thienocarboxy)-L-glutamide (gT)

2-Thiophenecarboxilic acids (0.217 g, 1.69 mmol), triethylamine (0.187 mL, 1.69 mmol) and *N*,*N*′-didodecyl-L-glutamide (***g***)[21] were dissolved in THF (100 mL) at 0 °C. Diethyl cyanophosphonate (DEPC, 1.251 mL, 1.69 mmol) was added to the mixture. After being stirred for 1 day at room temperature, the solution was concentrated in vacuo. The residue was redissolved in chloroform (50 mL), and the organic layer was washed three times with 0.5 N NaOH (50 mL) and 0.5 N HCl (30 mL), then washed with water (30 mL) and dried with sodium sulfate. The solution was concentrated in vacuo, and the residue was purified by recrystallization from acetonitrile to give **gT** as white powders (60%): mp 120–121 °C. Anal. Calcd for $C_{34}H_{61}O_3N_3S$: C, 69.0; H, 10.4; N, 7.10. Found: C, 68.8; H, 10.3; N, 7.10. FT-IR (KBr) 3300, 3092, 2921, 2851, 1641, 1622, 1540, 1467, 1375, 1292, and 713 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ 0.88 (6H, t, J = 7 Hz, $-CH_3$), 1.25 (36H, br s, $-(CH_2)_9-$), 1.47–1.52 (2H, m, $-CH_2CH_2(CH_2)_9-$),

2.14–2.19 (2H, m, –CHCH_2CH$_2$–), 2.31–2.61 (2H, m, –(C=O)CH_2CH$_2$–), 3.22–3.28 (4H, m, –NHCH_2CH$_2$–), 4.48 (1H, q, J = 6 Hz, –CH–), 5.88 (1H, t, J = 5 Hz, –NH–), 6.93 (1H, t, J = 6 Hz, –NH–), 7.10 (1H, t, J = 4 Hz, –CHCH=CHS–), 7.50 (1H, d, J = 4 Hz, –CH=CHCH–), 7.65 (1H, d, J = 4 Hz, –SCH=CH–), and 8.07 (1H, d, J = 6 Hz, –NH–); ^{13}C NMR (400 MHz; $CDCl_3$; Me_4Si) δ 14.12, 22.70, 26.91, 28.55, 29.28, 29.55, 31.93, 33.08, 39.72, 39.90, 53.40, 127.8, 128.5, 130.6, 138.8, 162.4, 171.0, 173.

Synthesis of *N*,*N*′′-didodecyl-N′-(2-benzo[3,4-*b*]thienocarboxy)-L-glutamide (*g*BT)

g*BT** was prepared by the coupling reaction of 2-benzo[3,4-*b*]thienocarboxylic acid and ***g. Recrystallization from acetone gave ***g*BT** as white powders (71%): mp 149–150 °C. Anal. Calcd for $C_{38}H_{63}O_3N_3S$: C, 71.09; H, 9.89; N, 6.55. Found: C, 70.87; H, 10.29; N, 6.58. FT-IR (KBr) 3327, 3248, 3067, 2953, 2919, 2850, 1653, 1638, 1577, 1543, 1467, 1352, 1325, 1249, 1216, and 719 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ 0.88 (6H, t, J = 7 Hz, –CH_3), 1.24 (36H, br s, –(CH_2)$_9$–CH$_3$), 1.47–1.52 (4H, m, –NHCH$_2$CH_2–), 2.17–2.23 (4H, m, –CHCH_2CH$_2$–), 2.34–2.64 (2H, m, –(C=O)CH_2CH$_2$–), 3.27 (4H, q, J = 7 Hz, –NHCH_2 CH$_2$–), 4.52 (1H, q, J = 6 Hz, –CH–), 5.82–5.85 (1H, t, J = 6 Hz, –NH–), 6.93 (1H, t, J = 6 Hz, –NH–), 7.38–7.45 (2H, m, –CH= CHCH=CH–), 7.85–7.89 (3H, m, –CHCHCCHC(C=O)– and –SCCH =CH–), and 8.24 (1H, d, J = 6 Hz, –NH–). ^{13}C NMR (400 MHz; $CDCl_3$; Me_4Si) δ 14.12, 22.70, 26.90, 28.48, 29.28, 29.65, 31.93, 33.11, 39.73, 39.95, 53.60, 122.7, 124.1, 124.8, 125.2, 125.5, 126.4, 138.4, 139.2, 141.2, 162.8, 170.9, 173.3.

Synthesis of *N*,*N*′′-didodecyl-*N*′-(5-terthionocarboxy)-L-glutamide (*g*T$_3$)

g*T$_3$** was prepared by the coupling reaction of 2,2′:5′,2′′-terthiophene-5-carboxylic acid[22] with ***g. Reprecipitation from a chloroform solution to *n*-hexane gave ***g*T$_3$** as yellow powders (38%): mp 179–180 °C. Anal. Calcd for $C_{42}H_{65}O_3N_3S_3 + H_2O$: C, 65.87; H, 8.92; N, 5.24. Found: C, 66.19; H, 8.63; N, 5.59. FT-IR (KBr) 3305, 3099, 2955, 2920, 2850, 1656, 1631, 1543, 1523, 1468, 1443, 1317, and 799 cm^{-1}; ^{1}H (400 MHz; $CDCl_3$; Me_4Si) δ 0.87 (6H, t, J = 7 Hz, –CH_3), 1.24 (36H, br s, –(CH_2)$_9$–CH$_3$), 1.47–1.52 (4H, m, –NHCH$_2$CH_2–), 2.14–2.20 (4H, m, –CHCH_2CH$_2$–), 2.31–2.62 (2H, m, –(C=O)CH_2CH$_2$–), 3.25 (4H, q, J = 7 Hz, –NHCH_2CH$_2$–), 4.47 (1H, q, J = 6 Hz, –CH–), 5.81 (1H, t, J = 6 Hz, –NH–), 6.87 (1H, t, J = 6 Hz, –NH–), 7.04 (1H, dd, J = 4, 3 Hz, –C=CHCH=CHS–), 7.10 (1H, d, J = 3 Hz, –CH=CHS–), 7.13 (1H, d, J = 4 Hz, –C=CHCH=CHS–), 7.16 (1H, d, J = 4 Hz, –C=CHCH=C–), 7.20 (1H, d, J = 4 Hz, –C=CHCH=C–), 7.24 (1H, d, J = 4 Hz, –(C=O)C=CHCH=C–), 7.54 (1H, d, J = 3 Hz, –(C=O)C=CHCH=C–), and 8.10 (1H, d, J = 7 Hz, –NH–); ^{13}C NMR (400 MHz; $CDCl_3$; Me_4Si) δ 14.12, 22.70, 26.89, 28.40, 29.37, 29.68, 31.93, 33.12, 39.89, 53.40, 123.8, 124.1, 124.5, 125.0, 125.6, 128.0, 129.3, 132.4, 135.2, 135.6, 137.9, 139.7, 162.3, 171.0, 173.3.

Acknowledgment

This work was supported in part by the Japan Society for the Promotion of Science of the Ministry of Education, Science, Sports and Culture of Japan.

Supplementary data

Supplementary data (synthesis and characterization of tiophene-derivatives. Experimental details: solubility properties, and TEM measurements) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.07.006.

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