

# Synthesis of Bridged Oligothiophenes: Toward a New Class of Thiophene-Based Electroactive Surfactants

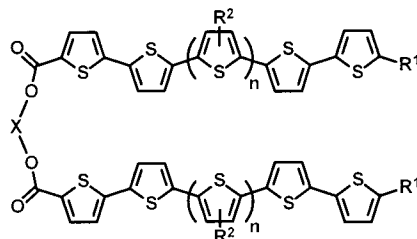
Carine Edder and Jean M. J. Fréchet\*<sup>†</sup>

Department of Chemistry, University of California–Berkeley,  
Berkeley, California 94720-1460, and Lawrence Berkeley National Laboratory,  
Materials Science Division, Berkeley, California 94720

frechet@cchem.berkeley.edu

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## ABSTRACT



A series of bridged oligothiophenes have been synthesized. Their novel molecular architecture, comprising two oligothiophenes linked together by a bridge at one  $\alpha$ -extremity and one binding group at the other  $\alpha$ -extremity, is expected to improve their utility as electroactive surfactants for semiconducting nanoparticles or organic electronics.

Polythiophene-based solar cells currently attract much attention.<sup>1</sup> Indeed, their electronic properties such as relatively large hole mobilities and absorption in the visible region<sup>2</sup> make them good candidates as hole conductors and/or sensitizers for such systems. Recently, the blend of the conjugated polymer poly(3-hexylthiophene) (P3HT) with CdSe nanoparticles was successfully used in an organic–inorganic hybrid solar cell.<sup>1d</sup> Further improvements of this

system are likely to result if the interaction of the components at the nanocrystal–polymer interface can be enhanced. A first step in this direction was recently accomplished when penta(3-hexylthiophene)-2-phosphonic acid was used as a surfactant for CdSe nanoparticles.<sup>3</sup> The strong affinity of the phosphonic acid group for the CdSe surface allowed efficient coating of the nanocrystals, resulting in enhanced solubility in nonpolar solvents. Moreover, excitation to the CdSe nanoparticles induced an efficient charge separation at the interface, revealing the potential of an oligothiophene surfactant as a mediator component in polymer–nanocrystal devices.

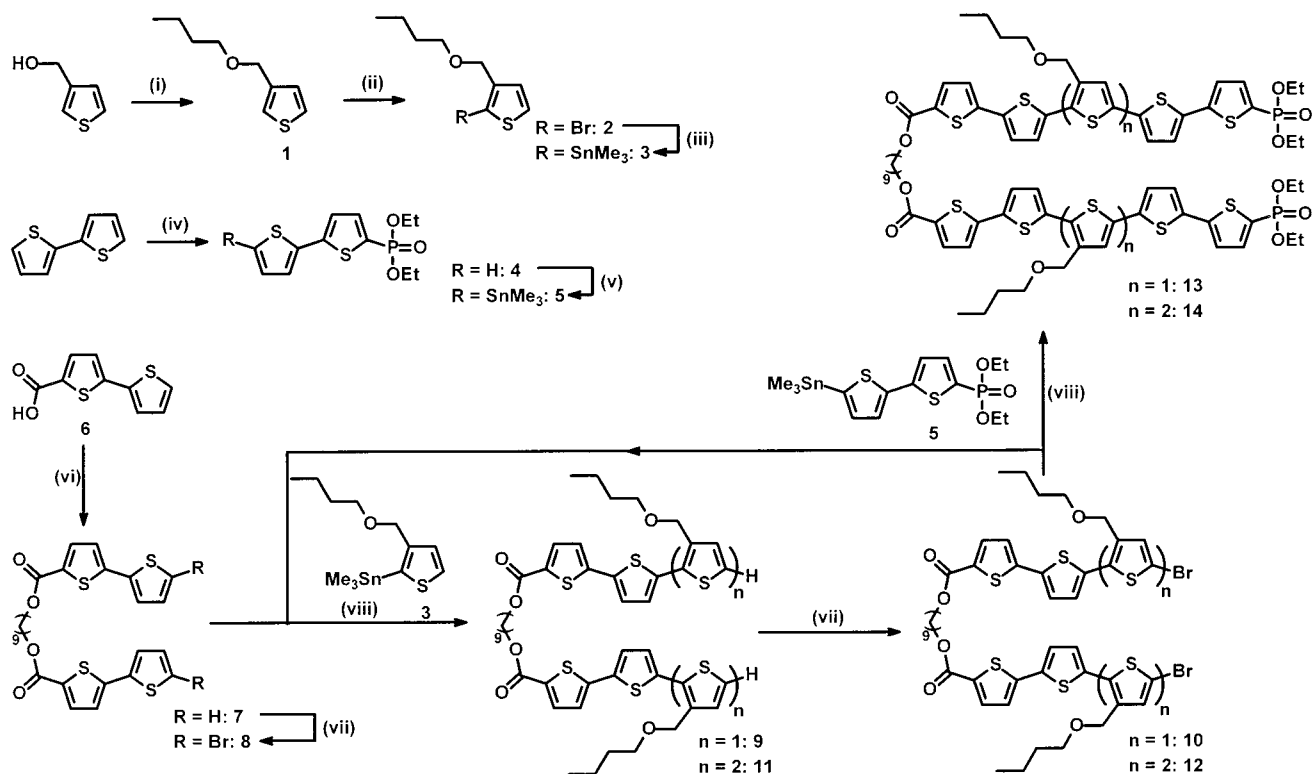
During routine preparation,<sup>4</sup> CdSe nanoparticles are commonly capped with organic ligands such as trioctylphosphine oxide. Therefore, surfactants with a stronger affinity for the

<sup>†</sup> www.frechet.com

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(2) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed; Wiley-CH: Weinheim, Germany, 1999.

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Scheme 1<sup>a</sup>

<sup>a</sup> Reagents and conditions (yield): (i) (a) NaH, THF, 0 °C; (b) 1-bromobutane,  $\Delta$  (84%). (ii) NBS, CH<sub>3</sub>CO<sub>2</sub>H (66%). (iii) (a) *n*BuLi, THF, -78 °C, 90 min; (b) Me<sub>3</sub>SnCl (91%). (iv) (a) *n*BuLi, THF, -78 °C, 2 h; (b) ClP(O)(OEt)<sub>2</sub> (63%). (v) (a) LDA, THF, -78 °C, 90 min; (b) Me<sub>3</sub>SnCl (89%). (vi) 1,9-Dibromononane, K<sub>2</sub>CO<sub>3</sub>, 18C6, THF,  $\Delta$ , 3 days (89%). (vii) NBS, DMF, CHCl<sub>3</sub> (**8**, 95%; **10**, 96%; **12**, 81%). (viii) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, DMF, THF,  $\Delta$  (**9**, 68%; **11**, 70%; **13**, 34%; **14**, 10%).

nanocrystals are necessary to allow an efficient displacement of this insulating organic layer. Inspired by metal–ligand coordination chemistry, several groups have begun investigating the use of dithiol<sup>5</sup> or diazaperylene<sup>6</sup> surfactants, expecting a chelate effect to favor the surfactant–CdSe interaction. We have now designed a bidentate ligand composed of two tethered oligothiophenes, each containing one binding group. This molecular architecture is expected to facilitate binding to and organization around the nanocrystal. In particular, we expect favorable effects from the intramolecular  $\pi$ -stacking interaction between the two oligothiophene units of the bidentate molecule. The new design of thiophene-based electroactive surfactants links two oligothiophene backbones containing at least five thiophene units by a bridge located at one  $\alpha$ -extremity of each oligothiophene moiety. Binding groups with a strong affinity for CdSe nanoparticles are then introduced at the other  $\alpha$ -extremities, in direct conjugation with the oligothiophene moieties.

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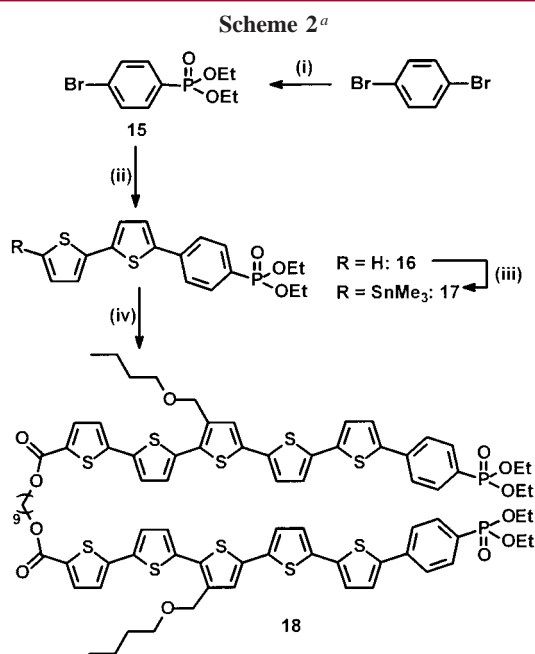
Finally, the solubility of the entire assembly is adjusted by introducing one or more substituents on the oligothiophene backbone.

Taking into account all these design features, compound **13** was selected as our first target (Scheme 1). A long (C9) alkyl chain was chosen for the bridge as it adds both solubility and flexibility to the molecule. The ester group at the  $\alpha$ -position not only plays the role of a linker to the bridge, but also acts as a protecting group at this position, allowing the oligomer chain to grow exclusively from the other  $\alpha$ -position.<sup>7</sup> The other  $\alpha$ -extremity was functionalized with a diethylphosphonate group, useful in its own right but also a potential precursor of the strongly binding phosphonic acid moiety.<sup>8</sup> Finally, instead of the alkyl chains commonly chosen for solubility,<sup>2</sup> we substituted alkoxy chains since their higher polarity facilitated chromatographic purification.

Our synthetic approach relies upon the synthesis of three building blocks: the bridged bis(bithiophene) (Scheme 1, **7**), the  $\beta$ -substituted monothiophene (**1**), and the bithiophene bearing the diethylphosphonate at one of its  $\alpha$ -positions (**4**).

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(8) McKenna, C. E.; Higa, M. T.; Cheung, N. H.; McKenna, M.-C. *Tetrahedron Lett.* **1977**, *2*, 155.

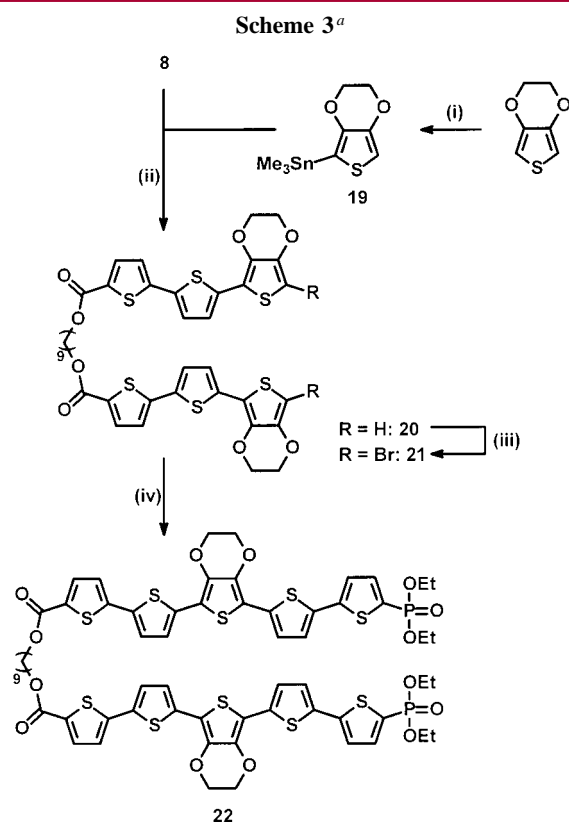


<sup>a</sup> Reagents and conditions (yield): (i) (a) Mg (1.1 equiv), THF; (b)  $\text{ClP(O)(OEt)}_2$  (22%). (ii) 5-(Trimethylstannyl)-2,2'-bithiophene,  $\text{PdCl}_2(\text{PPh}_3)_2$ , DMF, THF,  $\Delta$  (69%). (iii) (a) LDA (2 equiv), TMEDA, THF,  $-78^\circ\text{C}$ , 90 min (99%); (b)  $\text{Me}_3\text{SnCl}$ . (iv) **10**,  $\text{PdCl}_2(\text{PPh}_3)_2$ , DMF, THF,  $\Delta$  (10%).

A Stille-type coupling reaction was chosen to connect the thiophene subunits, because of its compatibility with both carbo- and phosphoester groups. Side reactions such as homocoupling and loss of functionalization are inherent to metal-catalyzed cross-coupling reactions; therefore, isolation of pure oligothiophenes is often tedious and requires extensive chromatographic purification.<sup>2</sup> Our synthetic strategy takes advantage of the polarity differences of the three building blocks to simplify purification. Thus, the bis(pentathiophene) **13** was prepared according to the strategy described in Scheme 1. Regioselective bromination of **1** using *N*-bromosuccinimide (NBS), followed by transmetalation with *n*-butyllithium (*n*BuLi) and subsequent quenching with trimethyltin chloride, afforded **3**. The phosphonate **4** was obtained by lithiation of 2,2'-bithiophene and quenching of the anion with diethylchlorophosphate. The tin reagent **5** was similarly prepared by lithiation of **4** with lithium diisopropylamide (LDA), followed by quenching with trimethyltin chloride. The bridged bis(bithiophene) **7** was easily obtained by reaction of 2,2'-bithiophene carboxylic acid **6**<sup>7a</sup> with 1,9-dibromononane in the presence of 18-crown-6. Bromination of **7** at the  $\alpha$ -position using NBS gave the dibrominated compound **8**, which was then coupled with the tin reagent **3** to afford **9**. Bromination of this compound, followed by coupling with **5**, finally gave the bis(pentathiophene) **13**. The bis(sexithiophene) **14** was prepared from **10** using a second sequence of coupling–bromination reactions as applied for **10**, followed by a final Stille-coupling reaction with **5**.

Having demonstrated the feasibility of our synthetic strategy with **13** and its extension to the longer bis-

(sexithiophene) **14**, we were interested in modifying components of our system, i.e., backbone and bridge, to obtain a variety of bidentate systems displaying different electronic and geometric properties. For this purpose, a benzene ring was introduced in the conjugated backbone, as in **18** (Scheme 2), and the  $\beta$ -substituent was modified, as in **22** (Scheme 3). Only four additional steps were necessary to obtain **18**

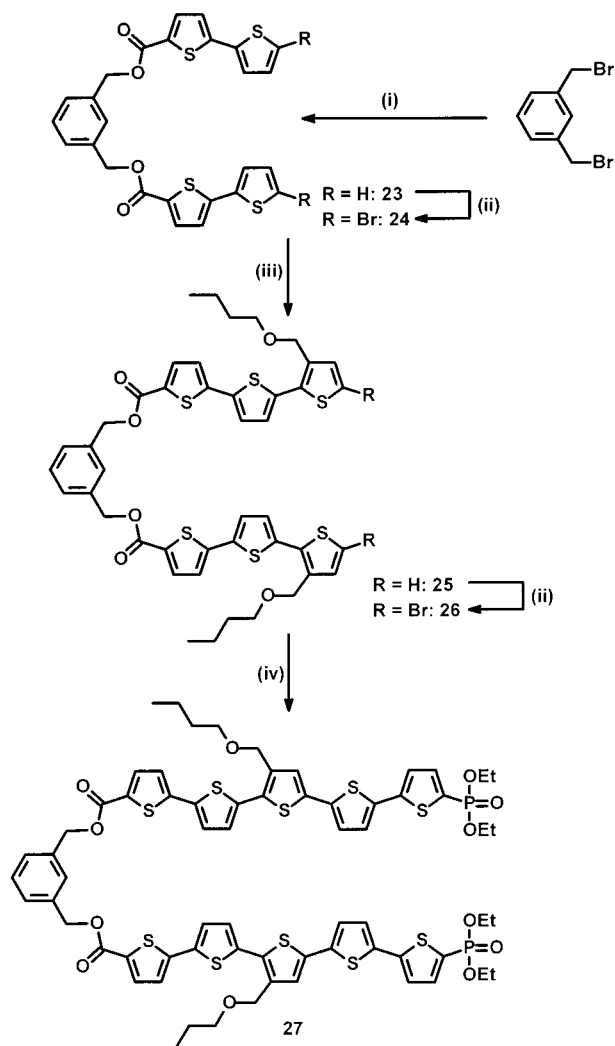


<sup>a</sup> Reagents and conditions (yield): (i) (a) *n*BuLi, THF,  $-78^\circ\text{C}$  to rt, 1 h; (b)  $\text{Me}_3\text{SnCl}$  (89%). (ii)  $\text{PdCl}_2(\text{PPh}_3)_2$ , DMF, THF (70%). (iii) NBS, DMF, THF (98%). (iv) **5**,  $\text{PdCl}_2(\text{PPh}_3)_2$ , DMF, THF,  $\Delta$  (57%).

from **10** and *p*-dibromobenzene. The phosphonate **15** was prepared by reacting the Grignard reagent of *p*-dibromobenzene with diethylchlorophosphate. Cross-coupling reaction of **15** with 5-(trimethylstannyl)-2,2'-bithiophene<sup>9</sup> gave **16**. The stannate **17** was prepared by quenching the LDA-generated anion of **16** with trimethyltin chloride. Coupling with **10** finally gave the bis(pentathiophene) **18**. The low yield associated with this reaction, as observed for **14**, suggests either a solubility problem or an intramolecular interaction between the two oligomer units that precludes an efficient heterocoupling reaction and leads to the formation of a significant amount of byproducts.

Replacement of the alkoxy chain in **13** by the strong donor group present in **22** is expected to significantly affect the

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Scheme 4<sup>a</sup>

<sup>a</sup> Reagents and conditions (yield): (i) **6**, K<sub>2</sub>CO<sub>3</sub>, 18C6, THF, Δ, 3 days (82%). (ii) NBS, DMF, CHCl<sub>3</sub> (**24**, 93%; **26**, 93%). (iii) **3**, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, DMF, THF, Δ (75%). (iv) **5**, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, DMF, THF, Δ (11%).

electronic properties of this molecule, which is prepared as shown in Scheme 3. The stannate **19** was obtained by

lithiation of 3,4-ethylenedioxythiophene with *n*BuLi and subsequent quenching with trimethyltin chloride. It was then coupled with **8** to afford **20**. Bromination, followed by coupling reaction with **5**, finally gave the new bridged molecule **22**.

A more rigid bridge may be necessary to avoid the intermolecular cross-linking of two nanoparticles by the same surfactant. The *m*-xylene linker used in **27** is more predisposed to provide the desired conformation to the molecular system than the long alkyl chain previously used, without being too rigid, as in the bis(quaterthiophene) systems based on 1,8-naphthalene linker.<sup>10</sup> The new molecule **27** was prepared by esterification of **6** with α,α'-dibromo-*m*-xylene, followed by two successive bromination/coupling reactions, according to the same approach as described for **13** (Scheme 4).

In summary, the synthetic strategy described in this paper has been successfully used to obtain a variety of oligothiophenes, displaying a novel molecular architecture based on the linkage of twin oligothiophenes in the same molecule. Structural modifications of the backbone or the bridge group enables the tuning of the electronic and geometric properties of these bridged molecules. Further investigation of these systems involves their application as surfactants for nanocrystals and electroactive components for organic-based electronics and photovoltaic systems.

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**Supporting Information Available:** Complete details for the synthesis and characterization of compounds **1–5** and **7–27**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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