JOC Article

Novel Synthesis of Protected Thiol End-Capped Stilbenes and Oligo(phenylenevinylene)s (OPVs)

Nicolai Stuhr-Hansen, Jørn B. Christensen, Niels Harrit, and Thomas Bjørnholm*

Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

tb@nano.ku.dk

Received August 31, 2002

The first general procedures for preparation of thiol end-capped stilbenes and oligo(phenylenevinylene)s (OPVs) with *tert*-butyl- and acetyl-protected thiol termini have been developed. These reactions proceed via Br/Li exchange, McMurry, and Wittig-type reactions. The thiol functionality is protected against strong basic and acidic reaction conditions as a *t*-Bu sulfide. As a key point in the method, reprotection of the thiol group is accomplished by means of acetyl chloride and boron tribromide. The novel strategy forms the basis for stepwise introduction of 4-mercaptostyryl units in OPVs. The new mono-, di-, and trimercapto OPVs have potential applications as one, two, and three terminal molecular devices in gold nanoparticle clusters, self-assembled monolayers, and optoelectronic devices.

Introduction

Much current research is devoted to the study of charge transport through organic materials.[1] These efforts are inspired by phenomena and applications such as electroluminescence and light-emitting diodes (LEDs).[2,3] Conductivity measurements on individual molecules require an electronic coupling between the "molecular wire" and the metal electrodes. This can be accomplished through terminal thiol groups that have high affinity to gold.[4] Thus, dithiol functionalized oligo(phenyleneethynylenes)[5−8] and terthiophene[9] have been mounted as wires between gold electrodes. Related investigations have been performed on thiol-terminated oligo(phenyleneethynylenes)[10] and oligothiophenes.[11,12]

Repeating phenylenevinylene units have not been investigated in this respect until the recently reported work by Dudek et al.,[13] who prepared asymmetric OPVs with ferrocene on one end and methyl thiol on the other end, making them capable of self-assembly on gold electrodes. However, common to the synthetic procedures applied there and reported syntheses of other thiol-terminated systems (such as oligo(1,4-phenylene ethynylene)s[5,6,14−16] and oligo(2,5-thiophene ethynylene)s[17]) is the introduction of the protected thiol groups at the very end of the synthetic sequence.

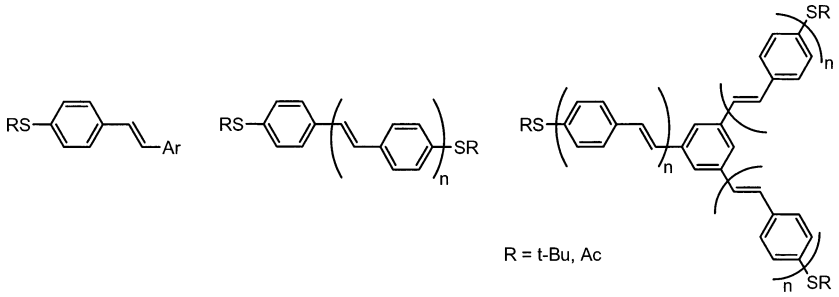
The present work adopts a different approach. In this case aryl thiol functionality is introduced as the *t*-Bu sulfide at the beginning of the synthetic sequences and maintained through the following steps owing to the resistance of *t*-Bu-S-Ar to both strongly basic and acidic conditions. In order for this principle to be useful, the strong protection group must be converted into a more reactive functionality, which is easily removable in situ prior to, e.g., self-assembly experiments, while still protecting the conjugated thiol against oxidation by air. The Ac group meets these two demands. Thus, as a final step the *t*-BuS group is converted into the AcS moiety by means of $AcCl/BBr_3$ following our recently described method.[18]

With this protection strategy, we have applied several classic synthetic methods as means for obtaining the OPV

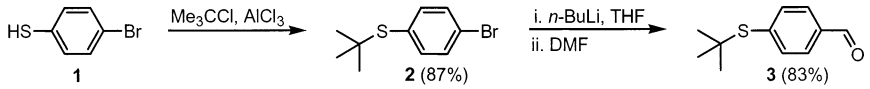
(1) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, 1998.
(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.
(3) Friend, R. H.; Greenham, N. C. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 823.
(4) Yaliraki, S. N.; Kemp, M.; Ratner, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 3428.
(5) Novak, J. P.; Brousseau, I. L. C.; Vance, F. W.; Johnson, R. C.; Lemon, B. I.; Hupp, J. T.; Feldheim, D. L. *J. Am. Chem. Soc.* **2000**, *122*, 12029.
(6) Tour, J. M.; Jones, I. L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.
(7) Creager, S.; Yu, C. J.; Bamdad, C.; O'Connor, S.; MacLean, T.; Lam, E.; Chong, Y.; Olsen, G. T.; Luo, J.; Gozin, M.; Kayyem, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1059.
(8) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C. W.; Chen, J.; Wang, W.; Campbell, I. *Chem.—Eur. J.* **2001**, *7*, 5118.
(9) Kergueris, C.; Bourgoin, J. P.; Palacin, S. *Nanotechnology* **1999**, *10*, 8.
(10) Dhirani, A. A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319.
(11) Hicks, R. G.; Nodwell, M. B. *J. Am. Chem. Soc.* **2000**, *122*, 6746.
(12) Purcell, S. T.; Garcia, N.; Binh, V. T.; Jones, L., II; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11985.
(13) Dudek, S. P.; Sikes, H. D.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2001**, *123*, 8033.
(14) Fan, F.-R. F.; Yang, Y.; Dirk, S. M.; Price, D. W.; Kosynkin, D.; Tour, J. M.; Bard, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 2454.
(15) Jones, L., II; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388.
(16) Novak, J. P.; Feldheim, D. L. *J. Am. Chem. Soc.* **2000**, *122*, 3979.
(17) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.
(18) Stuhr-Hansen, N. *Synth. Commun.* 2002, in press.

10.1021/jo0263770 CCC: $25.00
Published on Web 01/09/2003

CHART 1



SCHEME 1



carbon structures. Among them, Wittig[19−24] and Horner−Wadsworth−Emmons (HWE)[25−28] reactions are well described as efficient routes to OPVs and substituted stilbenes. Usually, various amounts of *cis*-stilbenes are produced,[29] but all-*trans* conversion can be accomplished as part of the recrystallization procedure. Although *t*-Bu sulfides proved to be perfectly resistant to the strong basic reaction conditions involved in these standard methods, the thioester group would have been cleaved. The presence of free thiols also would not have been possible, since they react with aldehydes leading to polymeric material.[30]

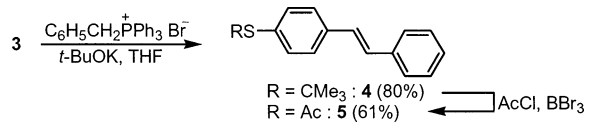
Other methods that are used successfully in this work include McMurry[24] and Knoevenagel[31,32] reaction procedures. Again, thioesters would have been absolutely intolerable, whereas these methods proved fully compatible with *t*-Bu sulfide protection.

The new compounds presented in this work are represented by the three general structures shown in Chart 1.

Results and Discussion

***tert*-Butylthio- and Acetylthio-Substituted Stilbenes.** 4-(*tert*-Butylthio)benzaldehyde[18,33] (**3**, Scheme 1) served as the essential precursor for a number of 4-mercapto end-capped OPVs. It was prepared from commercially available 4-bromothiophenol (**1**), which was reacted with 2-chloro-2-methylpropane in the presence of a catalytic amount of aluminum chloride. The resulting 4-bromophenyl *tert*-butyl sulfide[34] (**2**) was lithiated using BuLi and subsequently treated with DMF to give **3** in high yield.

SCHEME 2



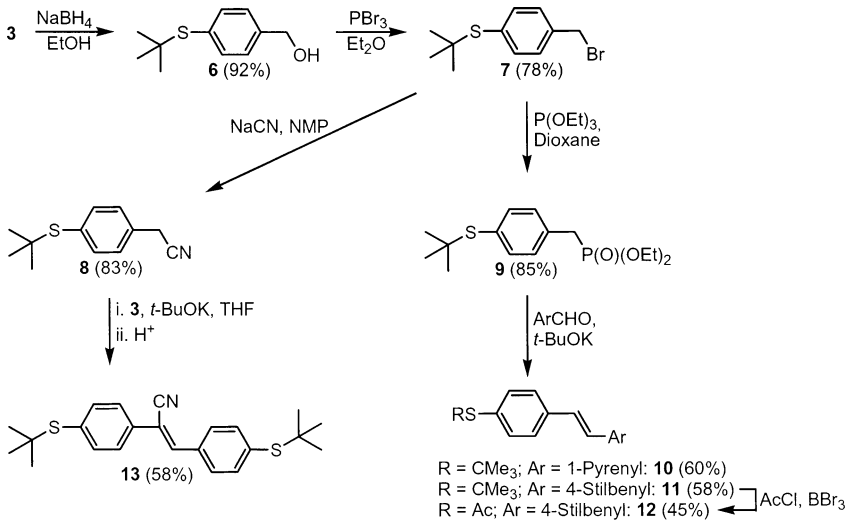
Protected thiol end-capped stilbenes can be obtained from aldehyde **3** by conventional Wittig reactions.[35,36] Thus, addition of *t*-BuOK to a slurry of **3** and benzyltriphenylphosphonium bromide (Scheme 2) produced *trans*-4-(*tert*-butylthio)stilbene (**4**), which was easily converted into *trans*-(*S*-acetyl)-4-stilbenethiol (**5**) by means of AcCl/BBr_3 following the recently described procedure.[18]

In principle, an asymmetrical alkene can be prepared by two routes following the so-called umpolung strategy as illustrated in Scheme 3. Aldehyde **3** was reduced with $NaBH_4$ to afford 4-(*tert*-butylthio)benzyl alcohol (**6**) in excellent yield. This was cleanly converted into 4-(*tert*-butylthio)benzyl bromide (**7**) using PBr_3. Importantly, there was no acid-induced *t*-Bu/S bond cleavage observed during the benzyl bromide synthesis. Compound **7** was converted into two *p*-mercaptostyryl end-block synthetic equivalents, that is, (i) 4-(*tert*-butylthio)benzyl cyanide (**8**) by reaction with sodium cyanide, and (ii) diethyl 4-(*tert*-butylthio)benzylphosphonate (**9**) via an Arbuzov reaction with triethyl phosphite (Scheme 3).

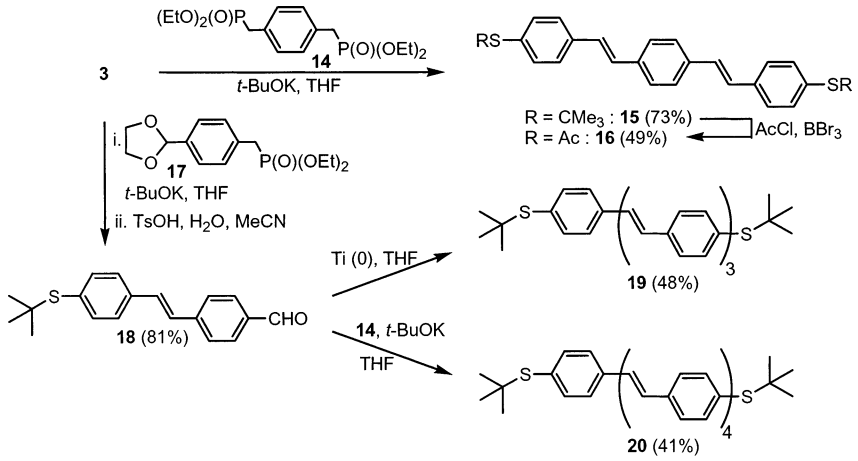
1-Pyrenecarboxaldehyde and 4-stilbenecarboxaldehyde were used as model systems for generation of 4-(*tert*-butylthio)styryl compounds by HWE reaction with **9** upon *t*-BuOK treatment. The reaction was quenched with water, and the raw product was isolated by filtration. Following all-*trans* conversion (iodine in boiling toluene), (*E*)-1-[4-(*tert*-butylthio)styryl]pyrene (**10**) and (*E*,*E*)-4-[4-(*tert*-butylthio)styryl]stilbene (**11**), respectively, were obtained.

(19) Campbell, T. W.; McDonald, R. N. *J. Org. Chem.* **1959**, *24*, 1246.
(20) Drehfahl, G.; Kühmstedt, R.; Oswald, H.; Hörhold, H.-H. *Makromol. Chem.* **1970**, *131*, 89.
(21) Gill, R. E.; Meetsma, A.; Hadziioannou, G. *Adv. Mater.* (*Weinheim, Ger.*) **1996**, *8*, 212.
(22) Kossmehl, G.; Härtel, M.; Manecke, G. *Makromol. Chem.* **1970**, 37.
(23) Rumi, M.; Ehrlich, J. E.; Heikal, A. A.; Perry, J. W.; Barlow, S.; Hu, Z.; McCord-Maughon, D.; Parker, T. C.; Röckel, H.; Thayumanavan, S.; Marder, S. R.; Beljonne, D.; Brédas, J.-L. *J. Am. Chem. Soc.* **2000**, *122*, 9500.
(24) Schenk, R.; Gregorius, H.; Meerholz, K.; Heinze, J.; Müllen, K. *J. Am. Chem. Soc.* **1991**, *113*, 2634.
(25) Cho, B. R.; Chajara, K.; Oh, H. J.; Son, K. H.; Jeon, S.-J. *Org. Lett.* **2002**, *4*, 1703.
(26) Diez-Barra, E.; Garcia-Martinez, J. C.; Rodriguez-Lopes, J. *Tetrahedron Lett.* **1999**, *40*, 8181.
(27) Diez-Barra, E.; Garcia-Martinez, J. C.; Merino, S.; del Rey, R.; Rodriguez-Lopez, J.; Sanchez-Verdu, P.; Tejeda, J. *J. Org. Chem.* **2001**, *66*, 5664.
(28) Segura, J. L.; Gomez, R.; Martin, N.; Guldi, D. M. *Org. Lett.* **2001**, *3*, 2645.
(29) Vedejs, E.; Fleck, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 5861.
(30) Friedländer, P.; Lenk, E. *Chem. Ber.* **1912**, *45*, 2083.
(31) Detert, H.; Sugiono, E. *J. Phys. Org. Chem.* **2000**, *13*, 587.
(32) Stalmach, U.; Detert, H. *J. Prakt. Chem.* **2000**, *342*, 10.
(33) Dickman, D. A.; Chemburkar, S.; Konopacki, D. B.; Elisseou, E. M. *Synthesis* **1993**, 573.
(34) Adams, R.; Ferretti, A. *J. Am. Chem. Soc.* **1959**, *81*, 4927.
(35) Ludley, F.; Breitmaier, E. *Synthesis* **1994**, 949.
(36) Manecke, G.; Lüttke, S. *Chem. Ber.* **1970**, *103*, 700.

SCHEME 3



SCHEME 4



The reaction of **10** with AcCl/BBr_3 did not afford 2-[4-(acetylthio)styryl]pyrene, because monoacetylation of the pyrene ring system occurred simultaneously, resulting in isolation of 1-[4-(acetylthio)styryl]-3-acetylpyrene. Obviously, the reactivity of the pyrene system illustrates a limitation in the reprotection procedure. In contrast, none of the OPVs obtained in this work were acetylated on carbon by the Ac^+ formed from the AcCl/BBr_3 reagent couple. Low solubility was another obstacle met in reprotection reactions. For example, *t*-BuS-OPV **11** was never completely converted according to TLC, even though dilution and elongated reaction time gave higher degrees of reactant consumption. However, (*E*,*E*)-4-[4-(acetylthio)styryl]stilbene (**12**) was purified by means of liquid chromatography.

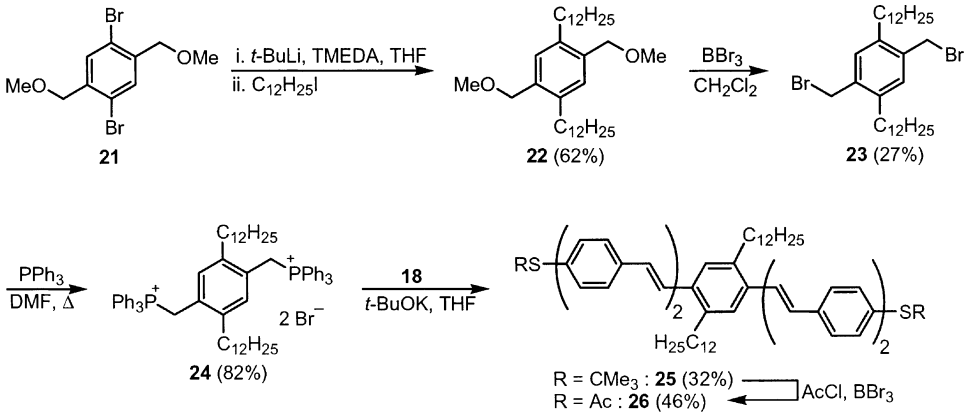
Among other applications, OPVs with electron-donating end-groups and an electron-accepting middle section are interesting for their nonlinear optical properties.[37] To prepare such a model system with sulfide end groups, a Knoevenagel reaction was carried out between **8** and **3** in the presence of *t*-BuOK (Scheme 3). After acidification, (*Z*)-2,3-bis[4-(*tert*-butylthio)phenyl]acrylonitrile (**13**) was isolated. Unfortunately, the corresponding bis-AcS compound, 2,3-bis[4-acetylthio)phenyl]acrylonitrile, could not be obtained in satisfactory purity. The cyano stilbene tended to decompose during attempted reprotection with AcCl/BBr_3.

***tert*-Butylthio- and Acetylthio-Substituted Long Chain OPVs.** *t*-BuS end-capped 1,4-distyrylbenzene can be obtained in a reaction between **3** and the difunctional HWE reagent tetraethyl 1,4-xylylenediphosphonate (**14**) when treated with *t*-BuOK in THF (Scheme 4). Pure (*E*,*E*)-1,4-bis[4-(*tert*-butylthio)styryl]benzene (**15**) was isolated in good yield after isomerization (iodine in toluene) into the all-*trans* OPV isomer. During conversion of **15** into (*E*,*E*)-1,4-bis[4-(acetylthio)styryl]benzene (**16**) high dilution and extended reaction times were required to avoid precipitation of unreacted starting material.

Stepwise elongation of an OPV chain with one styryl unit can be accomplished with the new reagent diethyl 4-(1,3-dioxolan-2-yl)benzylphosphonate (**17**) (Scheme 4). Thus, alkene formation occurred smoothly by treatment of aldehyde **3** with **17** and *t*-BuOK. This reaction is generally applicable, efficient, and convenient, since the phosphorus products formed are water-soluble in contrast to earlier methods. Upon acetal cleavage with water/*p*-

(37) Albota, M.; Beljonne, D.; Bredas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X. L.; Xu, C. *Science (Washington, D.C.)* **1998**, *281*, 1653.

SCHEME 5



toluenesulfonic acid followed by reflux in toluene in the presence of a catalytic amount of iodine, (*E*)-4-(*tert*-butylthio)styrylbenzaldehyde (**18**) was isolated in high yield. Importantly, the *tert*-butylthio group survived the acidic acetal cleavage conditions, and the yield of purified **18** remained comparable to the raw yield of the acetal-protected precursor.

Proceeding from compound **18**, a McMurry[18] coupling was undertaken (Scheme 4). The reaction occurred smoothly, but purification was hampered by the insolubility generally met among long unbranched OPVs.[38] However, Soxhlet extraction provided (*E*,*E*,*E*)-4,4′-bis[4-(*tert*-butylthio)styryl]stilbene (**19**) in sufficient purity. One additional styryl unit could be introduced in a typical HWE-reaction between **18** and **14**. Water quenching and filtration provided the raw (*cis*/*trans*) product in good yield. This was completely insoluble in common solvents but (*E*,*E*)-1,4-bis[4-{(*E*)-4-(*tert*-butylthio)styryl}styryl]-benzene (**20**) was obtained in 41% yield after Soxhlet extraction (chlorobenzene/I_2). Compounds **19** and **20** could not be converted into the corresponding bis-AcS compounds because of solubility problems.

Alkyl-Substituted OPVs. To obtain soluble OPV dithiols, a synthetic procedure was developed for preparation of the alkyl-substituted OPV (*E*,*E*)-1,4-bis[4-{(*E*)-4-(acetylthio)styryl}styryl]-2,5-didodecylbenzene (**26**) (Scheme 5). 1,4-Dibromo-2,5-bis(methoxymethyl)benzene[39] (**21**) reacted with 4 equiv of *t*-BuLi in TMEDA/THF during warm-up from dry ice to room temperature. 1,4-Bis(methoxymethyl)-2,5-dilithiobenzene was formed as a white precipitate, which remained stable at room temperature under argon for several hours. No sign of polymerization was observed, nor during preparation and handling of the unsubstituted 1,4-dilithiobenzene in model experiments, in contrast to observations reported in the literature.[40] In a substitution reaction with 1-iodododecane, 1,4-bis(methoxymethyl)-2,5-didodecylbenzene (**22**) was smoothly isolated. Since the reactivity of dilithiobenzenes has only been sparsely investigated,[40] this procedure for attachment of two alkyl chains to one benzene ring is a new method of broad scope.

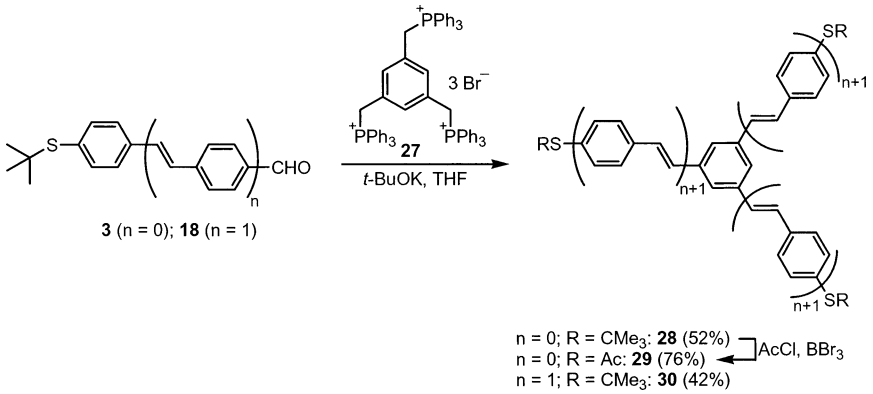
Treatment of **22** with BBr_3 established the benzylic bromide functions in 1,4-bis(bromomethyl)-2,5-didodecylbenzene (**23**), which was easily converted into the corresponding bis-phosphonium salt [1,4-didodecyl-2,5-bis(triphenylphosphoniomethyl)benzene] dibromide (**24**) by reaction with triphenylphosphine. A classical Wittig reaction between the bis-ylide of **24** and **18** gave the soluble (*E*,*E*)-1,4-bis[4-{(*E*)-4-(*tert*-butylthio)styryl}styryl]-2,5-didodecylbenzene (**25**) (Scheme 5). The high solubility of **25** in organic solvents facilitated *t*-Bu/Ac exchange and isolation of (*E*,*E*)-1,4-bis[4-{(*E*)-4-(acetylthio)styryl}styryl]-2,5-didodecylbenzene (**26**).

***tert*-Butylthio- and Acetylthio-Substituted 1,3,5-Tristyrylbenzenes.** Three-terminal molecular systems have potential applications as the central building block in gold particle trimers.[16] To obtain thiol end-capped 1,3,5-tristyrylbenzenes,[26−28,41] **3** was reacted with [1,3,5-tris(triphenylphosphoniomethyl)benzene] tribromide[42] (**27**) (Scheme 6) upon treatment with *t*-BuOK forming (*E*,*E*,*E*)-1,3,5-tris[(4-(*tert*-butylthio)styryl]benzene (**28**), which was easily purified by simple means. Upon *t*-Bu/Ac exchange using AcCl/BBr_3, (*E*,*E*,*E*)-1,3,5-tris[(4-(acetylthio)styryl]-benzene (**29**) was isolated in high purity. The 1,3,5-substitution pattern made this molecular system much more soluble than the linearly unsubstituted 1,4-OPVs. Thus, further elongation was performed without encountering serious solubility problems. The 4-formylstilbenyl elongated aldehyde **18** reacted with tris-ylide **27**, and the second-generation molecule (*E*,*E*,*E*)-1,3,5-tris[4-{(*E*)-4-(*tert*-butylthio)styryl}styryl]benzene (**30**) was isolated, being the first 1,3,5-tris(4-stilbenylvinyl)benzene reported. However, it has not yet been possible to isolate the corresponding tris-AcS compound (*E*,*E*,*E*)-1,3,5-tris-[4-{(*E*)-4-(acetylthio)styryl}styryl]benzene.

Characterization of OPVs. All ^{1}H NMR spectra obtained (and displayed in Supporting Information) of the final recrystallization products **4**, **5**, **10**, **11**, **15**, **16**, **18**, **25**, **26**, **28**, **29**, and **30** are consistent with the all-*trans* stereoisomers[21] as the only species present. An X-ray crystal structure[43] obtained of **29** shows that all four benzene rings are coplanar, while the acetyl groups are twisted out of plane. Because of solubility problems, ^{1}H NMR spectra could not be obtained from compounds **12**, **19**, and **20**. However, by analogy, these oligomers are believed to exist in all-*trans* configuration too.[21] ^{13}C NMR

(38) van Hutten, P. F.; Wildeman, J.; Meetsma, A.; Hadziioannou, G. *J. Am. Chem. Soc.* **1999**, *121*, 5910.
(39) Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662.
(40) Stephens, E. B.; Kinsey, K. E.; Davis, J. F.; Tour, J. M. *Macromolecules* **1993**, *26*, 3519.
(41) Meier, H.; Zertani, R.; Noller, K.; Oelkrug, D.; Krabichler, G. *Chem. Ber.* **1986**, *119*, 1716.
(42) Storck, W.; Manecke, G. *Makromol. Chem.* **1975**, *176*, 97.
(43) Larsen, K.; Magnussen, M.; Nielsen, S. F.; Soerensen, H. O.; Stuhr-Hansen, N. Unpublished work.

SCHEME 6



spectra from all soluble compounds are reproduced in Supporting Information. The individual absorptions are not listed and assigned in the Experimental Section because of the complexity of the spectra.

Many of the stilbenes and OPVs prepared in the course of this work display intense fluorescence. Together with absorption data, their maximum emission wavelengths are reported in the Experimental Section.

Conclusions

Implementation of *t*-Bu as protecting group for the thiol functionality allows synthetic procedures to be carried out under extremely basic and acidic conditions. In combination with classical methods such as Horner−Wadsworth−Emmons reactions and McMurry couplings, a range of new *t*-BuS-substituted stilbenes and OPVs have been prepared. The combination of an umpolung strategy and building-block principles allows for selection of the best synthetic route to a specific OPV in consideration of available starting materials.

Usually, the *t*-Bu group is converted into the versatile AcS group by means of $AcCl/BBr_3$. Introductions of long alkyl substituents circumvent the solubility problems usually encountered among long unbranched OPV chains and render these new compounds promising candidates for elements in future nanocircuits and supramolecular systems. Investigations of their electrical and optical properties are in progress.

Experimental Section

4-(*tert*-Butylthio)benzyl alcohol (6). To a mixture of 4-(*tert*-butylthio)benzaldehyde (**3**)[18,33] (5.83 g, 30 mmol) and EtOH (80 mL) cooled in an ice bath was added $NaBH_4$ (1.25 g, 33 mmol) in small portions during a 10 min period. The reaction mixture was stirred at room temperature for 1 h and then poured into ice (150 g) containing hydrochloric acid (4 M, 50 mL), followed by extraction with petroleums ether (3 × 40 mL). The organic layer was washed with water, dried over anhydrous $MgSO_4$, and filtered. Removal of solvent in vacuo gave the benzyl alcohol **6** (5.41 g, 92%) as a colorless oil, which crystallized into white crystals upon standing at room temperature. Mp: 40−42 °C. Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.21. Found: C, 67.18; H, 8.32. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.27 (s, 9H), 2.84 (br.s, 1H), 4.63 (s, 2H), 7.28 (d, J = 6.4 Hz, 2H), 7.48 (d, J = 6.4 Hz, 2H). GC-MS: EI (*m*/*z*, relative intensity) 196 (M^+, 15), 181 (3), 140 (100).

4-(*tert*-Butylthio)benzyl bromide (7). To a mixture of 4-(*tert*-butylthio)benzyl alcohol (**6**) (2.94 g, 15 mmol) in Et_2O (30 mL) cooled in an ice bath was added phosphorus tribromide (4.60 g, 17 mmol) in a dropwise fashion during a 10 min period. The reaction mixture was stirred at room temperature for 1 h and then poured into ice (100 g). The layers were separated, and the aqueous phase was further extracted with Et_2O (2 × 25 mL). The organic layer was washed with water (10 mL), dried over anhydrous $MgSO_4$, and filtered. Removal of solvent in vacuo gave a white crystalline material, which upon recrystallization from heptane afforded the benzyl bromide **7** (3.02 g, 78%) as white needles. Mp: 59−60 °C. Anal. Calcd for $C_{11}H_{15}BrS$: C, 50.97; H, 5.83; S, 12.37. Found: C, 51.39; H, 5.81; S, 12.40. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.29 (s, 9H), 4.49 (s, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H). GC-MS: EI (*m*/*z*, relative intensity) 260 (M^+, 3), 204 (11), 179 (7), 123 (100).

4-(*tert*-Butylthio)benzyl Cyanide (8). 4-(*tert*-Butylthio)-benzyl bromide (**7**) (1.30 g, 5 mmol) was added to a slurry of sodium cyanide (1.30 g, 5.5 mmol) in 1-methyl-2-pyrrolidinone (10 mL). The reaction mixture was stirred at room temperature for 12 h and then poured into sodium carbonate (10% aq, 50 mL) and extracted with Et_2O (3 × 15 mL). The combined etheral phases were washed with water and filtered through basic alumina (10 g) by means of Et_2O. Removal of solvent in vacuo gave the benzyl cyanide as a crystalline material, which upon recrystallization from heptane gave **8** (0.85 g, 83%) as white needles. Mp: 68−69 °C. Anal. Calcd for $C_{12}H_{15}NS$: C, 70.20; H, 7.36; N, 6.82; S, 15.61. Found: C, 70.40; H, 7.52; N, 6.82; S, 15.62. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.26 (s, 9H), 3.74 (s, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.52 (d, J = 7.9 Hz, 2H). GC-MS: EI (*m*/*z*, relative intensity) 205 (M^+, 12), 190 (3), 149 (100).

Diethyl 4-(*tert*-Butylthio)benzylphosphonate (9). A solution of 4-(*tert*-butylthio)benzyl bromide (**7**) (5.18 g, 20 mmol) and triethyl phosphite (4.15 g, 25 mmol) in dioxane (30 mL) was refluxed under nitrogen for 12 h. The solvent was evaporated in vacuo, and bulb-to-bulb distillation (100 Pa, air bath 130 °C) gave the 4-mercaptostyryl precursor **9** (5.38 g, 85%) as a colorless liquid. Anal. Calcd for $C_{15}H_{25}O_3PS$: C, 56.94; H, 7.96; S, 10.13. Found: C, 56.60; H, 7.96; S, 9.87. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (t, J = 7.0 Hz, 6H), 1.20 (s, 9H), 3.09 (d, J = 21.8 Hz, 2H), 3.90−3.98 (m, 4H), 7.21 (dd, J = 2.4, 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H). GC-MS: EI (*m*/*z*, relative intensity) 316 (M^+, 13), 260 (100), 232 (26).

(*Z*)-2,3-Bis[4-(*tert*-butylthio)phenyl]acrylonitrile (13). To a solution of 4-(*tert*-butylthio)benzaldehyde (**3**) (0.19 g, 1 mmol) and 4-(*tert*-butylthio)benzyl cyanide (**8**) (0.21 g, 1 mmol) in THF (10 mL) cooled in an ice/ethanol bath was added *t*-BuOK (0.12 g, 1.1 mmol) in small portions during a 10 min period. Stirring at room temperature was maintained for 1 h. The reaction mixture was diluted with hydrochloric acid (2 M, 25 mL), stirred for 10 min at room temperature, poured into water, and extracted with CH_2Cl_2/pentane (1:2, 3 × 20 mL). The organic layer was washed with water and filtered through silica gel (60F, 10 g) by means of CH_2Cl_2. Removal of solvent in vacuo gave a crystalline material, which was recrystallized

from heptane affording the α-cyanostilbene **13** (0.22 g, 58%) as yellow crystals. Mp: 100−102 °C. Anal. Calcd for $C_{23}H_{27}NS_2$: C, 72.39; H, 7.13; N, 3.67; S, 16.80. Found: C, 72.00; H, 7.06; N, 3.77; S, 16.59. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.32 (s, 9H), 1.33 (s, 9H), 7.58 (s, 1H), 7.59 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H). MS (FAB+): (M^+) 381.

Diethyl 4-(1,3-Dioxolan-2-yl)benzylphosphonate (17). A solution of 4-(1,3-dioxolan-2-yl)benzyl bromide[35] (7.29 g, 30 mmol) and triethyl phosphite (20 mL) was heated at 120 °C under nitrogen for 6 h. Excess phosphite was removed on a rotary evaporator, and bulb-to-bulb distillation (10 Pa, air bath 120 °C) gave **17** (7.71 g, 86%) as a colorless liquid. Anal. Calcd for $C_{14}H_{21}PO_5$: C, 56.00; H, 7.05. Found: C, 55.62; H, 7.00. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.17 (t, J = 7.1 Hz, 6H), 3.15 (d, J = 21.8 Hz, 2H), 3.94−4.05 (m, 4H), 4.07−4.14 (m, 4H), 5.78 (s, 1H), 7.31 (dd, J = 2.4, 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H). GC-MS: EI (*m*/*z*, relative intensity) 299 (M^+, 44), 271 (6), 255 (5), 228 (23), 91 (100).

***trans*-4-(*tert*-Butylthio)styrylbenzaldehyde (18).** To a mixture of diethyl 4-(1,3-dioxolan-2-yl)benzylphosphonate (**17**) (6.01 g, 20 mmol) and 4-(*tert*-butylthio)benzaldehyde (**3**) (3.89 g, 20 mmol) in THF (50 mL) cooled in an ice bath was added *t*-BuOK (2.47 g, 22 mmol) in small portions during a 10 min period. The reaction mixture was stirred at room temperature for 1 h and then poured into water (200 mL). A yellow crystalline material was filtered off, refluxed in a water/acetonitrile mixture (1:19, 200 mL) for 2 h in the presence of *p*-toluenesulfonic acid monohydrate (1.9 g, 10 mmol), and then poured into water (300 mL). After extraction with toluene (3 × 40 mL) the combined extracts were washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was boiled for 12 h in a solution of iodine in toluene (0.1 mM, 30 mL). Evaporation of the solvent followed by recrystallization from heptane gave the stilbenecarboxaldehyde **18** (4.78 g, 81%) as yellow crystals. Mp: 111−113 °C. Anal. Calcd for $C_{19}H_{20}OS$: C, 76.99; H, 6.80; S, 10.82. Found: C, 76.69; H, 6.85; S, 10.74. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H), 7.16 (d, J = 16.3 Hz, 1H), 7.25 (d, J = 16.3 Hz, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 10.00 (s, 1H). GC-MS: EI (*m*/*z*, relative intensity) 296 (M^+, 13), 281 (3), 240 (100).

***trans*-4-(*tert*-Butylthio)stilbene (4).** To a mixture of benzyltriphenylphosphonium bromide (1.94 g, 5 mmol) and 4-(*tert*-butylthio)benzaldehyde (**3**) (0.97 g, 5 mmol) in THF (30 mL) cooled in an ice bath was added *t*-BuOK (0.62 g, 5.5 mmol) in small portions during a 10 min period. The reaction mixture was stirred at room temperature for 1 h and then poured into water (100 mL). The phases were separated, and the water phase was further extracted with toluene (2 × 25 mL). The pooled organic phases were washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated. The product was separated by flash chromatography on silica gel 60F (30 g) by means of CH_2Cl_2. After evaporation of solvent the white crystalline product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling at room temperature the pure *trans*-stilbene crystallized, and filtration afforded **4** (1.08 g, 80%) as white plates. Mp: 164−165 °C. Anal. Calcd for $C_{18}H_{20}S$: C, 80.55; H, 7.51; S, 11.94. Found: C, 80.41; H, 7.55; S, 11.49. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H), 7.10 (d, J = 16.3 Hz, 1H), 7.15 (d, J = 16.3 Hz, 1H), 7.27 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.52−7.54 (m, 4H). GC-MS: EI (*m*/*z*, relative intensity) 268 (M^+, 22), 212 (100), 208 (4), 178 (39).

4-(*S*-Acetyl)stilbenethiol (5). To a solution of *trans*-4-(*tert*-butylthio)stilbene (**4**) (0.54 g, 2 mmol) and AcCl (1 mL) in CH_2Cl_2 (20 mL) was added BBr_3 (1.0 M solution in CH_2Cl_2, 2.2 mL, 2.2 mmol). Stirring was maintained for 2 h at room temperature. The dark reaction mixture was poured into ice (100 g), the phases were separated, and the water phase was further extracted with Et_2O/heptane (1:2, 2 × 20 mL). The pooled extracts were washed with water (40 mL), dried with magnesium sulfate, and concentrated. The residual material was boiled for 12 h in a solution of iodine in toluene (0.1 mM, 5 mL). After evaporation of the solvent, recrystallization from heptane gave the acetyl protected stilbenethiol **5** (0.31 g, 61%) as white plates. Mp: 153−155 °C. Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55; S, 12.60. Found: C, 75.36; H, 5.66; S, 12.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.10 (d, J = 16.3 Hz, 1H), 7.16 (d, J = 16.3 Hz, 1H), 7.28 (t, J = 7.3 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.51−7.55 (m, 4H). GC-MS: EI (*m*/*z*, relative intensity) 254 (M^+, 23), 212 (100), 178 (44).

***(E,E)*-4-[4-(*tert*-Butylthio)styryl]stilbene (11).** To a mixture of diethyl 4-(*tert*-butylthio)benzylphosphonate (**9**) (0.95 g, 3 mmol) and *trans*-4-stilbenecarboxaldehyde (0.62 g, 3 mmol) in THF (50 mL) cooled in an ice bath was added *t*-BuOK (0.37 g, 3.3 mmol) in small portions during a 10 min period. After stirring at room temperature for 1 h the reaction mixture was poured into water (200 mL). The product was filtered off, washed with water, dried, and dissolved in a limiting amount of boiling iodine solution in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling to room temperature the pure all-*trans* vinylene crystallized, and filtration afforded **11** (0.64 g, 58%) as white needles. Mp: 267−269 °C. Anal. Calcd for $C_{26}H_{26}S$: C, 84.28; H, 7.07; S, 8.65. Found: C, 84.02; H, 6.98; S, 8.52. MS: EI (*m*/*z*, relative intensity) 370 (M^+, 48), 314 (100), 279 (7).

***(E,E)*-4-[4-(Acetylthio)styryl]stilbene (12).** To a slurry of (*E*,*E*)-4-[4-(*tert*-butylthio)styryl]stilbene (**11**) (0.18 g, 0.5 mmol), AcCl (0.5 mL), CH_2Cl_2 (20 mL), and toluene (40 mL) was added BBr_3 (1.0 M solution in CH_2Cl_2, 0.55 mL, 0.55 mmol). After stirring for 12 h at room temperature under nitrogen, the dark reaction mixture was poured into water (200 mL), and the crystalline precipitate was filtered off, washed with water, and dried. The crystalline residue was boiled for 12 h in the minimum amount of a solution containing iodine in toluene (0.1 mM). By slow cooling at room temperature the protected vinylene thiol crystallized, and filtration gave **12** (0.08 g, 45%) as pale yellow plates. Mp: 268−270 °C (dec). Anal. Calcd for $C_{24}H_{20}OS$: C, 80.86; H, 5.65; S, 8.99. Found: C, 80.49; H, 5.58; S, 8.42. MS: EI (*m*/*z*, relative intensity) 356 (M^+, 69), 314 (100), 279 (7).

***(E)*-1-[4-(*tert*-Butylthio)styryl]pyrene (10).** To a mixture of diethyl 4-(*tert*-butylthio)benzylphosphonate (**9**) (0.95 g, 3 mmol) and 1-pyrenecarboxaldehyde (0.69 g, 3 mmol) in THF (50 mL) cooled in an ice bath was added *t*-BuOK (0.37 g, 3.3 mmol) in small portions during a 10 min period. After stirring at room temperature for 1 h the reaction mixture was poured into water (200 mL). The product was filtered off, washed with water, dried, and dissolved in a limiting amount of boiling iodine solution in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling to room temperature the pure all-t vinylene crystallized, and filtration afforded **10** (0.71 g, 60%) as yellow microcrystals. Mp: 174−175 °C. Anal. Calcd for $C_{28}H_{24}S$: C, 85.67; H, 6.16; S, 8.17. Found: C, 85.40; H, 6.16; S, 8.34. MS: EI (*m*/*z*, relative intensity) 392 (M^+, 68), 336 (100), 302 (29), 291 (14). ϵ_{387}^{ABS}(1,2-dichlorobenzene) = 4.22 × 10^4 M^{-1} cm^{-1}. λ_{max}^{FLU}(1,2-dichlorobenzene) = 435 (1.00), 459 (0.83) nm.

***(E,E)*-1,4-Bis[4-(*tert*-butylthio)styryl]benzene (15).** To a solution of 4-(*tert*-butylthio)benzaldehyde (**3**) (7.77 g, 40 mmol) and tetraethyl 1,4-xylylenediphosphonate (**14**)[44] (7.57 g, 20 mmol) in THF (200 mL) cooled in an ice bath was added *t*-BuOK (4.94 g, 44 mmol) in small portions during a 10 min period. The reaction mixture was further stirred at room temperature for 6 h under nitrogen and then poured into water (300 mL). A yellow material was filtered off, washed with water, and dried. The product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling at room temperature the pure *trans*-stilbene crystallized, and filtration

(44) Schwöppe, D.; Meier, H. *J. Prakt. Chem.* **2000**, *342*, 459.

afforded **15** (6.67 g, 73%) as light-yellow crystals. Mp: 268−270 °C. Anal. Calcd for $C_{30}H_{34}S_2$: C, 78.55; H, 7.47; S, 13.98. Found: C, 78.37; H, 7.46; S, 13.61. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (18H), 7.131 (s, 2H), 7.134 (s, 2H), 7.48 (d, J = 8.5 Hz, 4H), 7.52 (s, 4H), 7.53 (d, J = 8.5 Hz, 4H). MS: EI (*m*/*z*, relative intensity): 458 (M^+, 62), 402 (18), 346 (100), 312 (6). ϵ_{374}^{ABS}(1,2-dichlorobenzene) = 7.02 × 10^4 M^{-1} cm^{-1}. λ_{max}^{FLU}(1,2-dichlorobenzene) = 440 nm.

(*E*,*E*)-1,4-Bis[4-(acetylthio)styryl]benzene (16). To a solution of 4,4′-bis[4-(*tert*-butylthio)styryl]benzene (**15**) (0.92 g, 2 mmol) in AcCl (1 mL), CH_2Cl_2 (20 mL), and toluene (40 mL) was dropwise added BBr_3 (1.0 M solution in CH_2Cl_2, 4.4 mL, 4.4 mmol). Stirring was maintained for 12 h at room temperature. The dark reaction mixture was poured into ice (100 g). The phases were separated, and the water phase was further extracted with toluene (1:2, 2 × 20 mL). The pooled extracts were washed with water (40 mL), dried with magnesium sulfate, and concentrated. The residual material was separated by flash chromatography on silica gel 60F (60 g) by means of CH_2Cl_2. After evaporation of solvent the yellow crystalline product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling and filtration **16** (0.42 g, 49%) was obtained as light yellow plates. Mp: >300 °C. Anal. Calcd for $C_{26}H_{22}O_2S_2$: C, 72.53; H, 5.15. Found: C, 72.50; H, 5.16. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 6H), 7.11 (d, J = 16.3 Hz, 2H), 7.16 (d, J = 16.3 Hz, 2H), 7.41 (d, J = 8.2 Hz, 4H), 7.52 (s, 4H), 7.55 (d, J = 8.2 Hz, 4H). MS: EI (*m*/*z*, relative intensity) 430 (M^+, 87), 388 (50), 346 (100).

(*E*,*E*,*E*)-4,4′-Bis[4-(*tert*-butylthio)styryl]stilbene (19). To a suspension of low valent titanium[45] prepared by very slow addition of $TiCl_4$ (0.92 mL, 8.4 mmol) to a slurry of zink dust (1.10 g, 16.8 mmol) in THF (50 mL) at 0 °C under nitrogen was added 4-(*tert*-butylthio)styrylbenzaldehyde (**18**) (2.08 g, 7 mmol). After heating at reflux under nitrogen for 6 h the reaction mixture was diluted with water (200 mL) and extracted with CH_2Cl_2/toluene (1:2, 4 × 100 mL). The combined extracts were washed with water, dried over magnesium sulfate, and filtered. Evaporation af solvent gave a yellow slimy substance that was Soxhlet extracted with a boiling solution of iodine in chlorobenzene (0.1 mM, 100 mL) for 12 h. Cooling and filtration gave **19** (0.94 g, 48%) as a yellow microcrystalline powder. Mp: >300 °C. Anal. Calcd for $C_{38}H_{40}S_2$: C, 81.38; H, 7.19; S, 11.43. Found: C, 80.87; H, 7.09; S, 10.99. MS: EI (*m*/*z*, relative intensity) 560 (M^+, 92), 504 (24), 448 (100). ϵ_{398}^{ABS}(1,2-dichlorobenzene) = 9.2 × 10^4 M^{-1} cm^{-1}. λ_{max}^{FLU}(1,2-dichlorobenzene) = 444 (1.00), 469 (0.90) nm.

(*E*,*E*)-1,4-Bis[4-{(*E*)-4-(*tert*-butylthio)styryl}styryl]benzene (20). To a solution of 4-(*tert*-butylthio)styrylbenzaldehyde (**18**) (2.97 g, 10 mmol) and tetraethyl 1,4-xylylenediphosphonate (**14**)[44] (1.89 g, 5 mmol) in THF (100 mL) cooled in an ice bath was added *t*-BuOK (1.23 g, 11 mmol) in small portions during a 10 min period. The reaction mixture was further stirred at room temperature for 6 h under nitrogen and poured into water (300 mL). A yellow material was filtered off, washed with water, and dried. Soxhlet extraction with a boiling solution of iodine in chlorobenzene (0.1 mM) for 12 h, cooling, and filtration gave **20** (1.36 g, 41%) as yellow crystals. Mp: >300 °C. Anal. Calcd for $C_{46}H_{46}S_2$: C, 83.34; H, 6.99; S, 9.67. Found: C, 82.97; H, 7.04; S, 9.58. MS: EI (*m*/*z*, relative intensity) 662 (M^+, 100), 606 (16), 560 (40), 550 (47). ϵ_{409}^{ABS}(1,2-dichlorobenzene) = 5.7 × 10^4 M^{-1} cm^{-1}. λ_{max}^{FLU}(1,2-dichlorobenzene) = 459 (1.00), 485 (0.70) nm.

(*E*,*E*,*E*)-1,3,5-Tris[(4-(*tert*-butylthio)styryl]benzene (28). To a slurry of 4-(*tert*-butylthio)benzaldehyde (**3**) (1.17 g, 6 mmol) and [1,3,5-tris(triphenylphosphoniomethyl)benzene] tribromide[42] (**27**) (2.29 g, 2 mmol) in THF (50 mL) cooled in an ice bath was added *t*-BuOK (0.67 g, 6.6 mmol) in small portions during a 10 min period. The reaction mixture was stirred at room temperature for 12 h under nitrogen, poured into water (100 mL), and extracted with toluene (3 × 25 mL). The combined organic phases were washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated. The product was separated by flash chromatography on silica gel 60F (20 g) by means of CH_2Cl_2/pentane (1:2). After evaporation of solvent the white crystalline product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling **28** (0.67 g, 52%) crystallized as white needles. Mp: 207−209 °C. Anal. Calcd for $C_{42}H_{48}S_3$: C, 77.73; H, 7.45. Found: C, 77.30; H, 7.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 27H), 7.19 (s, 6H (alkene proton signals appearing at same chemical shift)), 7.51 (d, J = 8.5 Hz, 6H), 7.55 (d, J = 8.5 Hz, 6H), 7.57 (s, 3H). MS: EI (*m*/*z*, relative intensity) 648 (M^+, 78), 592 (20), 536 (25), 480 (100). ϵ_{330}^{ABS}(1,2-dichlorobenzene) = 8.37 × 10^4 M^{-1} cm^{-1}. λ_{max}^{FLU}(1,2-dichlorobenzene) = 404 (0.97), 421 (1.00) nm.

(*E*,*E*,*E*)-1,3,5-Tris[(4-(acetylthio)styryl]benzene (29). To a solution of 1,3,5-tris[(4-(*tert*-butylthio)styryl]benzene (**28**) (0.32 g, 0.5 mmol) and AcCl (1 mL) in CH_2Cl_2 (20 mL) was dropwise added BBr_3 (1.0 M solution in CH_2Cl_2, 1.6 mL, 1.6 mmol). Stirring was continued for 2 h at room temperature. The dark reaction mixture was poured into ice (100 g), the phases were separated, and the water phase was further extracted with toluene (1:2, 2 × 20 mL). The pooled extracts were washed with water (40 mL), dried with magnesium sulfate, and concentrated. The residual material was separated by flash chromatography on silica gel 60F (20 g) by means of CH_2Cl_2/pentane (1:1). After evaporation of solvent the yellow crystalline product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.01 M). Reflux was maintained for 12 h. Upon cooling and filtration **29** (0.23 g, 76%) was isolated as light yellow needles. Mp: 160−161 °C. Anal. Calcd for $C_{36}H_{30}O_3S_3$: C, 71.26; H, 4.98; S, 15.85. Found: C, 71.18; H, 4.85; S, 15.57. ^{1}H NMR (400 MHz, CDCl3): δ 2.45 (s, 9H), 7.19 (s, 6H (alkene proton signals appear at the same chemical shift)), 7.46 (d, J = 8.4 Hz, 6H), 7.57 (s, 3H), 7.58 (d, J = 8.4 Hz, 6H). MS: EI (*m*/*z*, relative intensity) 606 (M^+, 49), 564 (59), 522 (57), 480 (100). X-ray crystals were prepared by slow crystallization from an unsaturated toluene solution.

(*E*,*E*,*E*)-1,3,5-Tris[4-{(*E*)-4-(*tert*-butylthio)styryl}styryl]-benzene (30). To a slurry of 4-(*tert*-butylthio)styrylbenzaldehyde (**18**) (0.27 g, 0.9 mmol) and [1,3,5-tris(triphenylphosphoniomethyl)benzene] tribromide (**27**)[42] (0.34 g, 0.3 mmol) in THF (15 mL) cooled in an ice bath was added *t*-BuOK (0.11 g, 1 mmol) in small portions during a 10 min period. The reaction mixture was stirred at room temperature for 12 h under nitrogen, poured into water (100 mL), and extracted with toluene (3 × 25 mL). The combined organic phases were washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated. The product was separated by flash chromatography on silica gel by means of CH_2Cl_2/pentane (1:2). After evaporation of solvent the white crystalline product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling **30** (0.12 g, 42%) precipitated as a yellow powder. Anal. Calcd for $C_{66}H_{66}S_3$: C, 82.97; H, 6.96. Found: C, 83.04; H, 7.06. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 27H), 7.11 (d, J = 20.7 Hz, 3H), 7.12 (d, J = 19.0 Hz, 3H), 7.20 (d, J = 20.7 Hz, 3H), 7.21 (d, J = 19.0 Hz, 3H), 7.46−7.57 (m, 27H). MS (FAB+): (M^+) 956. ϵ_{377}^{ABS}(1,2-dichlorobenzene) = 1.72 × 10^5 M^{-1} cm^{-1}. λ_{max}^{FLU}(1,2-dichlorobenzene) = 420 (1.00), 440 (0.97) nm.

1,4-Bis(methoxymethyl)-2,5-didodecylbenzene (22). Dibromo-2,5-bis(methoxymethyl)benzene (**21**)[39] (4.86 g, 15 mmol) was added in one portion to a solution of *t*-BuLi (1.5 M in hexane, 40 mL, 60 mmol) and TMEDA (10 mL) in THF (100 mL) cooled in a dry ice/acetone bath under Ar. The reaction mixture was stirred at room temperature for 1 h. After few minutes at room temperature the dilithiosalt began to form as a white precipitate. The reaction mixture was cooled in a

(45) Elandaloussi, E. H.; Frere, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. *J. Am. Chem. Soc.* **1997**, *119*, 10774.

dry ice/acetone bath, while 1-iododododecane (9.78 g, 33 mmol) was added rapidly. After 1 h of stirring at room temperature for, water (350 mL) was added. The phases were separated, and the aqueous phase was further extracted with pentane (2 × 50 mL). The combined organic layers were washed with saturated sodium chloride (10 mL), dried over anhydrous $MgSO_4$, and filtered. Removal of solvent in vacuo gave a white crystalline material, which upon recrystallization from acetone afforded the bis(methoxymethyl) compound **22** (4.70 g, 62%) white crystals. Mp: 53−54 °C. Anal. Calcd for $C_{34}H_{62}O_2$: C, 81.21; H, 12.43. Found: C, 80.92; H, 12.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−0.90 (m, 6H), 1.26−1.37 (m, 36H), 1.54−1.59 (m, 4H), 2.57−2.61 (m, 4H), 3.38 (s, 6H), 4.44 (s, 4H), 7.14 (s, 2H). MS: EI (*m*/*z*, relative intensity) 503 (M^+, 9), 471 (100), 439 (72).

1,4-Bis(bromomethyl)-2,5-didodecylbenzene (23). To a solution of 1,4-bis(methoxymethyl)-2,5-didodecylbenzene (**22**) (4.02 g, 8 mmol) in CH_2Cl_2 (50 mL) was added BBr_3 (1.0 M solution in CH_2Cl_2, 18 mL, 18 mmol) in one portion. The reaction mixture was stirred at room temperature for 2 h and poured into water (200 mL). The phases were separated, and the aqueous phase was further extracted with pentane (2 × 50 mL). The combined organic layers were washed with saturated sodium chloride (10 mL), dried over anhydrous $MgSO_4$, and filtered. Removal of solvent in vacuo gave a white crystalline material. Recrystallization from acetonitrile gave **23** (1.31 g, 27%) as white plates. Mp: 96−97 °C. Anal. Calcd for $C_{32}H_{56}Br_2$: C, 63.99; H, 9.40. Found: C, 63.95; H, 9.48. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.86−0.91 (m, 6H), 1.27−1.39 (m, 36H), 1.58−1.70 (m, 4H), 2.63−2.69 (m, 4H), 4.50 (s, 4H), 7.15 (s, 2H). MS: EI (*m*/*z*, relative intensity) 600 (M^+, 9), 521 (44), 441 (12), 367 (17), 287 (19), 212 (100).

[1,4-Dididecyl-2,5-bis(triphenylphosphoniomethyl)-benzene] Dibromide (24). A solution of 1,4-bis(bromomethyl)-2,5-didodecylbenzene (**23**) (1.20 g, 2 mmol) and triphenylphosphine (1.15 g, 4.4 mmol) in DMF (20 mL) was heated at 130 °C for 12 h under nitrogen. Evaporation gave a white crystalline residue, which was dissolved in boiling acetonitrile (10 mL). Precipitation occurred slowly on addition of boiling EtOAc (30 mL). Filtration and drying afforded the bis-ylide synthetic equivalent **24** (1.85 g, 82%) as a white powder. Mp: 236−237 °C. Anal. Calcd for $C_{68}H_{86}Br_2P_2$: C, 72.59; H, 7.70. Found: C, 72.12; H, 7.78. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.63−0.67 (m, 6H), 0.81−0.89 (m, 12H), 0.97−1.00 (m, 4H), 1.09−1.13 (m, 4H), 1.21−1.30 (m, 20H), 1.58−1.62 (m, 4H), 4.97 (d, J = 14.3 Hz, 4H), 6.69 (s, 2H), 7.60−7.72 (m, 18H), 7.88−7.92 (m, 12H). MS: electrospray (*m*/*z*, relative intensity) 1046 ($M^{2+}Br^-$, 68), 482 (M^{2+},100).

(*E*,*E*)-1,4-Bis[4-{(*E*)-4-(*tert*-butylthio)styryl}styryl]-2,5-didodecylbenzene (25). To a mixture of [1,4-didodecyl-2,5-bis(triphenylphosphoniomethyl)benzene] dibromide (**24**) (1.13 g, 1 mmol) and 4-(*tert*-butylthio)styrylbenzaldehyde (**18**) (0.59 g, 2 mmol) in THF (20 mL) cooled in an ice bath was added *t*-BuOK (0.25 g, 2.2 mmol) in small portions during a 10 min period. The reaction mixture was stirred at room temperature for 1 h and poured into water (100 mL). The phases were separated, and the water phase was further extracted with CH_2Cl_2/pentane (1:2, 2 × 25 mL). The pooled organic phases were washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated. The product was separated by flash chromatography on silica gel 60F (30 g) by means of CH_2Cl_2.pentane (1:2). After evaporation of solvent the white crystalline product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. After gentle removal af solvent in vacuo the yellow residue was recrystallized from ethyl acetate giving the soluble OPV **25** (0.32 g, 32%) as light-yellow highly fluorescent microcrystals. Mp: 173−174 °C. Anal. Calcd for $C_{70}H_{94}S_2$: C, 84.11; H, 9.48; S, 6.41. Found: C, 83.79; H, 9.48; S, 6.58. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−0.89 (m, 6H), 1.27−1.28 (m, 32H), 1.32 (s, 18H), 1.37−1.43 (m, 4H), 1.60−1.66 (m, 4H), 2.75−2.79 (m, 4H), 7.04 (d, J = 16.1 Hz, 2H), 7.11 (d, J = 16.3 Hz, 2H), 7.16 (d, J = 16.3 Hz, 2H), 7.39 (d, J = 16.1 Hz, 2H), 7.45 (s, 2H), 7.48 (d, J = 8.4 Hz, 4H), 7.52 (d, J = 8.4 Hz, 4H), 7.53 (br-s, 8H (two aromatic proton signals appearing at same chemical shift)). MS (FAB+): (M^+ − isobutylene) 942. ϵ_{408}^{ABS}(1,2-dichlorobenzene) = 1.27 × 10^5 M^{-1} cm^{-1}. λ_{max}^{FLU}(1,2-dichlorobenzene) = 468 (1.00), 497 (0.67) nm.

(*E*,*E*)-1,4-Bis[4-{(*E*)-4-(acetylthio)styryl}styryl]-2,5-didodecylbenzene (26). To a solution of (*E*,*E*)-1,4-bis[4-{(*E*)-4-(*tert*-butylthio)styryl}styryl]-2,5-didodecylbenzene (**25**) (0.20 g, 0.2 mmol) and AcCl (0.5 mL) in CH_2Cl_2 (10 mL) was added BBr_3 (1.0 M solution in CH_2Cl_2, 0.5 mL, 0.5 mmol). Stirring was maintained for 2 h at room temperature. The dark reaction mixture was poured into ice (100 g), the phases were separated, and the water phase was further extracted with Et_2O/heptane (1:2, 2 × 15 mL). The pooled extracts were washed with saturated sodium chloride (aq, 20 mL), dried with magnesium sulfate, and concentrated. The product was separated by flash chromatography on silica gel 60F (10 g) by means of CH_2Cl_2. After evaporation of solvent the yellow oil was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). The residual material was boiled for 12 h in a solution of iodine in toluene (0.1 mM, 5 mL). After evaporation of the solvent, recrystallization from acetonitrile gave the alkyl-substituted Ac-protected OPV **26** (0.09 g, 46%) as yellow crystalline material without a defined melting point. The crystals soften gradually upon heating. Anal. Calcd for $C_{66}H_{82}O_2S_2$: C, 81.60; H, 8.51; S, 6.60. Found: C, 82.07; H, 8.59; S, 6.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−0.88 (m, 6H), 1.26−1.43 (m, 36H), 1.64−1.68 (s, 4H), 2.44 (s, 6H), 2.75−2.77 (m, 4H), 7.04 (d, J = 16 Hz, 2H), 7.11 (d, J = 16 Hz, 2H), 7.17 (d, J = 16 Hz, 2H), 7.38 (d, J = 12 Hz, 4H), 7.41 (s, 2H), 7.43 (d, J = 12 Hz, 2H), 7.53 (br-s, 8H), 7.56 (d, J = 8 Hz, 4H).

Acknowledgment. Financial support from the European Union under the IST program "NANOMOL" (contract IST-1999-12603) is gratefully acknowledged.

Supporting Information Available: Copies of ^{13}C and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0263770