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Column chromatographic purification free synthesis of long-chain monodisperse oligo(1,4-phenyleneethynylene)s: towards large-scale automatic synthesis of molecular wires

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Abstract—A facile, mild and rapid solid phase synthetic route free of column chromatographic purification to the synthesis of soluble monodisperse long-chain oligo(1,4-phenyleneethynylene)s is presented.

Recently, much attention has been paid to monodisperse, well-defined conjugated oligomers both as models for analogous bulk polymers and as candidates for molecular wires and molecular scale electronic devices.[1] Shape persistent oligo(1,4-phenyleneethynylene)s appear especially attractive due to their excellent main-chain rigidity and interesting electronic characteristics.[2] While short-chain oligo(1,4-phenyleneethynylene)s are usual model systems for studying electron transfer through molecular wires, oligo(1,4-phenyleneethynylene)s longer than 50 Å would be good candidates for molecular scale electronic devices as suggested by Aviram.[3] Many strategies have been developed for the synthesis of such long-chain oligo(1,4-phenyleneethynylene)s, among which solid phase synthetic method became more favourable owing to its several advantages including simplified purification as well as potential automatic synthesis.[4–6] Unfortunately, the synthetic routes previously reported were too tedious. In this report, we developed a facile, mild and rapid solid phase synthetic route without any column chromatographic purification for the synthesis of soluble monodisperse oligo(1,4-phenyleneethynylene)s up to ca. 60 Å, through rationally selecting the starting materials and efficiently designing the synthetic route. All reactions employed were simple and highly efficient. We believe this route represents the most efficient one for the synthesis of soluble long-chain monodisperse oligo(1,4-phenyleneethynylene)s up to now.

The synthetic route is outlined in Scheme 1. 4-Iodoaniline was converted to the diazonium tetrafluoroborate salts **1** in high yield.[7] 1,4-Diiodo-2,5-didodecyloxybenzene (compound **2**) was conveniently synthesized in large scale according to the previously well-established procedure.[8] Merrifield's resin was converted to resin **3** by reaction with degassed dry *n*-propylamine in a sealed vessel under argon at 70 °C for 3 days.[9] Compound **1** was attached to resin **3** in the presence of potassium carbonate at 0 °C to afford resin **4**, which was then coupled with trimethylsilylacetylene in the presence of Pd/Cu catalyst and then desilylation by treatment with tetrabutylammonium fluoride (TBAF) in THF at room temperature to give the resin-supported terminal acetylene **5**. Resin-supported 1,4-phenyleneethynylene dimer **6**, the desired 'starting monomer' for an iterative divergent/convergent strategy, was prepared by coupling resin **5** with compound **2** and trimethylsilylacetylene in sequence using the above Pd/Cu catalyst system. One-third of **6** underwent desilylation with TBAF to afford the resin **7**. The remaining two-thirds of **6** was treated with MeI at 115 °C for 24 h to afford liberated dimer **8**. Resin **7** was then coupled with all of the liberated iodide **8** under Pd/Cu cross coupling conditions to afford the resin-supported tetramer **9**. The sequence was repeated to generate the resin-supported octamer **12**. octamer **13** liberated from resin **12** by treatment with MeI at 115 °C for 12 h is about 60 Å and is quite soluble

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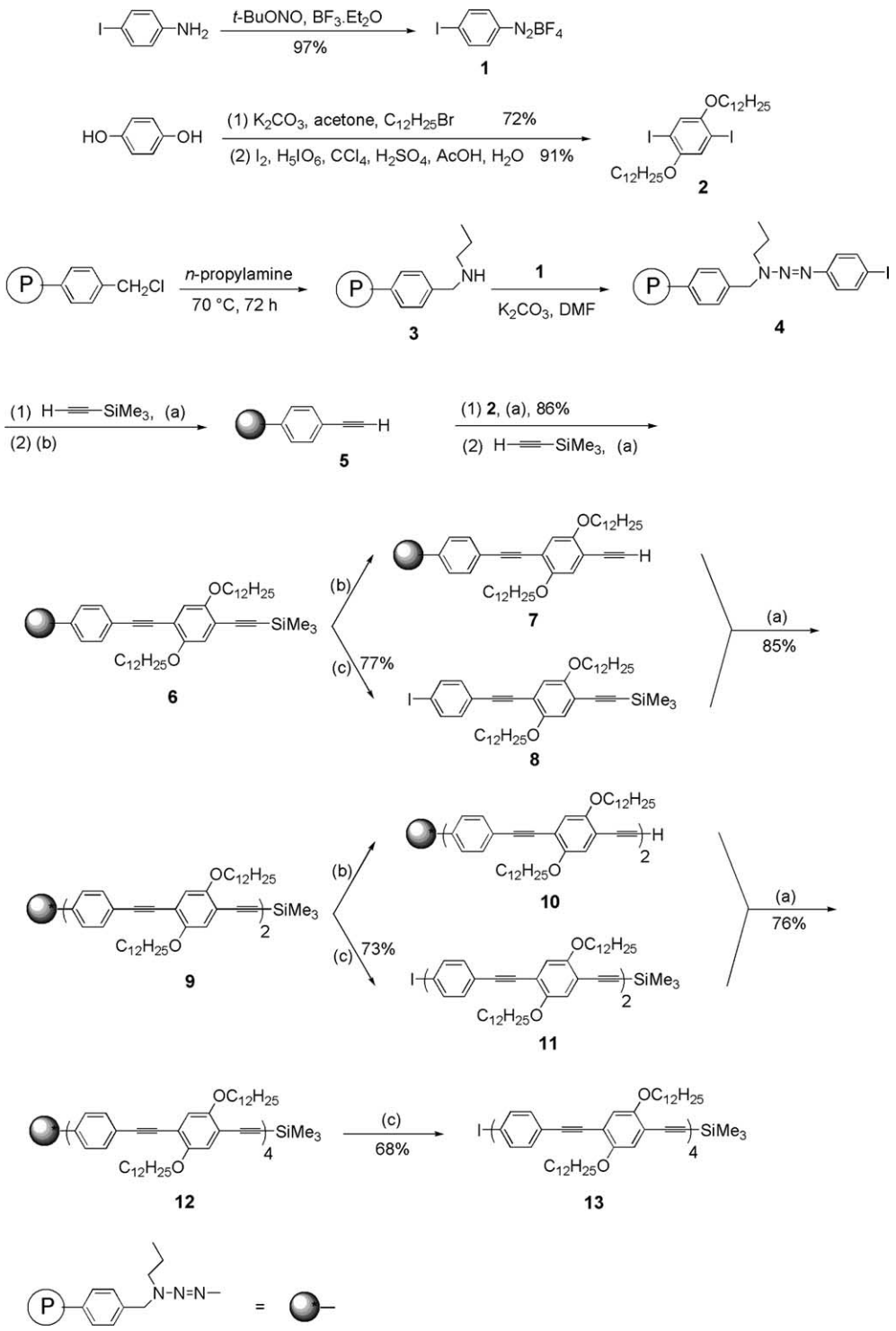

Scheme 1. The synthetic route to oligo(1,4-phenyleneethynylene)s. Reagents: (a) $Pd(dba)_2$, CuI, PPh_3, THF, Et_3N; (b) TBAF, THF; (c) MeI.

in common organic solvents such as THF, $CHCl_3$ and so on. Oligomers **8**, **11**, **13** were fully characterized by ^1H NMR, ^{13}C NMR, FTIR, elemental analysis and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS).[10] These oligomers were of good purity as judged by NMR and elemental analysis.

During the synthesis, each resin-supported reaction was monitored by FTIR analysis according to previously reported method.[5] Because yield calculations for solid phase synthesis were quite difficult, the yields marked in Scheme 1 were therefore only rough estimations based on the weight changes of the resin after each reaction.

Compared with previous solid phase synthetic route,[5] this new route has three main advantages: (1) it is more facile, because the 'starting monomer' for an iterative divergent/convergent strategy was simply synthesized

through fewer reaction steps, thus reducing the total reaction steps necessary to obtain the target oligomers. In fact, fussy synthesis of the 'starting monomer' was just the greatest shortcoming of previous solid phase synthetic route. In the present route, this shortcoming was overcome by choosing the substituted benzene rings that can be synthesized more easily than the substitution pattern in the previous route; (2) it is mild, because all reactions involved were easily-operative, especially, violent reagent *n*-BuLi, which was repeatedly needed in previous solid phase synthetic route was avoided; (3) most remarkably, the purification procedures are greatly simplified, because time-consuming column chromatographic purifications were not required throughout our synthesis process, since compounds **1** and **2** were easily purified by precipitation from the reaction mixtures without any further purification and by recrystallization, respectively, and all oligomers liberated from the resin were simply purified by passing the compounds through a silica gel plug. Due to the above advantages and the fact that all materials largely used were inexpensive and commercial available, this new route allows facile and large-scale synthesis of long-chain monodisperse oligo(1,4-phenyleneethynylene)s. Moreover, potential automatic synthesis of this type of molecular wires is also possible, mainly due to no need of column chromatographic purifications throughout the whole synthesis process.

In conclusion, a facile, mild and rapid solid phase synthetic route without any column chromatographic purifications was developed for the large-scale synthesis of soluble monodisperse long-chain oligo(1,4-phenyleneethynylene)s.

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10. Spectral data for oligomers: **8**. FTIR (KBr) 2955, 2920, 2851, 2154, 1503, 1469, 1411, 1389, 1275, 1249, 1217, 1033, 1006, 892, 860, 842, 815, 759, 721, 632 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.8$Hz, 2H), 6.94 (s, 2H), 3.97 (m, 4H), 1.81–1.79 (m, 4H), 1.51–1.50 (m, 4H), 1.33–1.26 (m, 32H), 0.90–0.86 (m, 6H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 154.15, 153.50, 137.49, 137.30, 133.00, 130.44, 122.96, 117.21, 116.76, 114.01, 113.77, 101.05, 100.27, 94.08, 93.82, 87.36, 69.53, 31.92, 29.70, 29.64, 29.43, 29.40, 29.35, 29.31, 26.05, 26.03, 22.69, 14.11. Anal. Calcd for $C_{43}H_{65}IO_2Si$: H, 8.53; C, 67.15. Found: H, 8.72; C, 66.83. MALDI-MS: 768 (M^+), 641 (M−I). Compound **11**. FTIR (KBr) 2920, 2851, 2151, 1515, 1496, 1469, 1412, 1383, 1278, 1248, 1218, 1071, 1004, 857, 836, 759 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz) δ 7.67 (d, $J = 7.2$ Hz, 2H), 7.49 (s, 4H), 7.25 (d, $J = 7.2$ Hz, 2H), 7.00 (s, 2H), 6.96 (s, 1H), 6.95 (s, 1H), 4.03–3.97 (m, 8H), 1.86–1.81 (m, 8H), 1.54–1.51 (m, 8H), 1.37–1.36 (m, 8H), 1.25 (br s, 56H), 0.89–0.85 (m, 12H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 154.16, 153.66, 153.51, 137.50, 133.02, 131.45, 123.28, 123.21, 122.97, 117.22, 116.82, 114.07, 113.95, 113.77, 101.09, 100.25, 94.78, 94.60, 94.11, 93.97, 87.89, 87.42, 69.60, 69.56, 69.49, 31.92, 29.65, 29.40, 29.36, 29.32, 26.05, 22.69, 14.12. Anal. Calcd for $C_{83}H_{121}IO_4Si$: H, 9.12; C, 74.51. Found: H, 9.32; C, 74.29. MALDI-MS: 1337 (M^+), 1264 (M−TMS), 1210 (M−I). Compound **13**. FTIR (KBr) 2921, 2851, 2150, 1517, 1490, 1469, 1414, 1386, 1278, 1218, 1072, 1004, 852, 835, 759, 719 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz) δ 7.69 (d, $J = 7.2$ Hz, 2H), 7.51–7.50 (m, 12H), 7.25 (d, $J = 7.2$ Hz, 2H), 7.02–7.00 (m, 6H), 6.96 (s, 1H), 6.95 (s, 1H), 4.05–3.97 (m, 16H), 1.87–1.82 (m, 16H), 1.56–1.53 (m, 16H), 1.39–1.36 (m, 16H), 1.25 (br s, 112H), 0.89–0.86 (m, 24H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 154.13, 153.64, 153.48, 137.47, 132.99, 131.43, 123.24, 122.95, 117.15, 116.78, 113.98, 113.74, 101.19, 100.20, 94.75, 94.60, 94.10, 93.96, 87.98, 87.42, 69.55, 69.43, 31.91, 29.69, 29.64, 29.41, 29.36, 29.31, 26.06, 22.68, 14.11. Anal. Calcd for $C_{163}H_{233}IO_8Si$: H, 9.49; C, 79.07. Found: H, 9.22; C, 78.76. MALDI-MS: 2476 (M+H), 2349 (M−I).