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Facile and Rapid Solid Phase Synthesis of Monodisperse Oligo(1, 4-phenyleneethynylene)s

Guo Rong LI, Xian Hong WANG*, Ji LI, Xiao Jiang ZHAO, Fo Song WANG

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences; Graduate School of the Chinese Academy of Sciences, Changchun 130022

Abstract: An extremely facile and rapid solid phase route free of column chromatographic purification for the synthesis of the soluble monodisperse oligo(1, 4-phenyleneethynylene)s up to ~60 Å was presented.

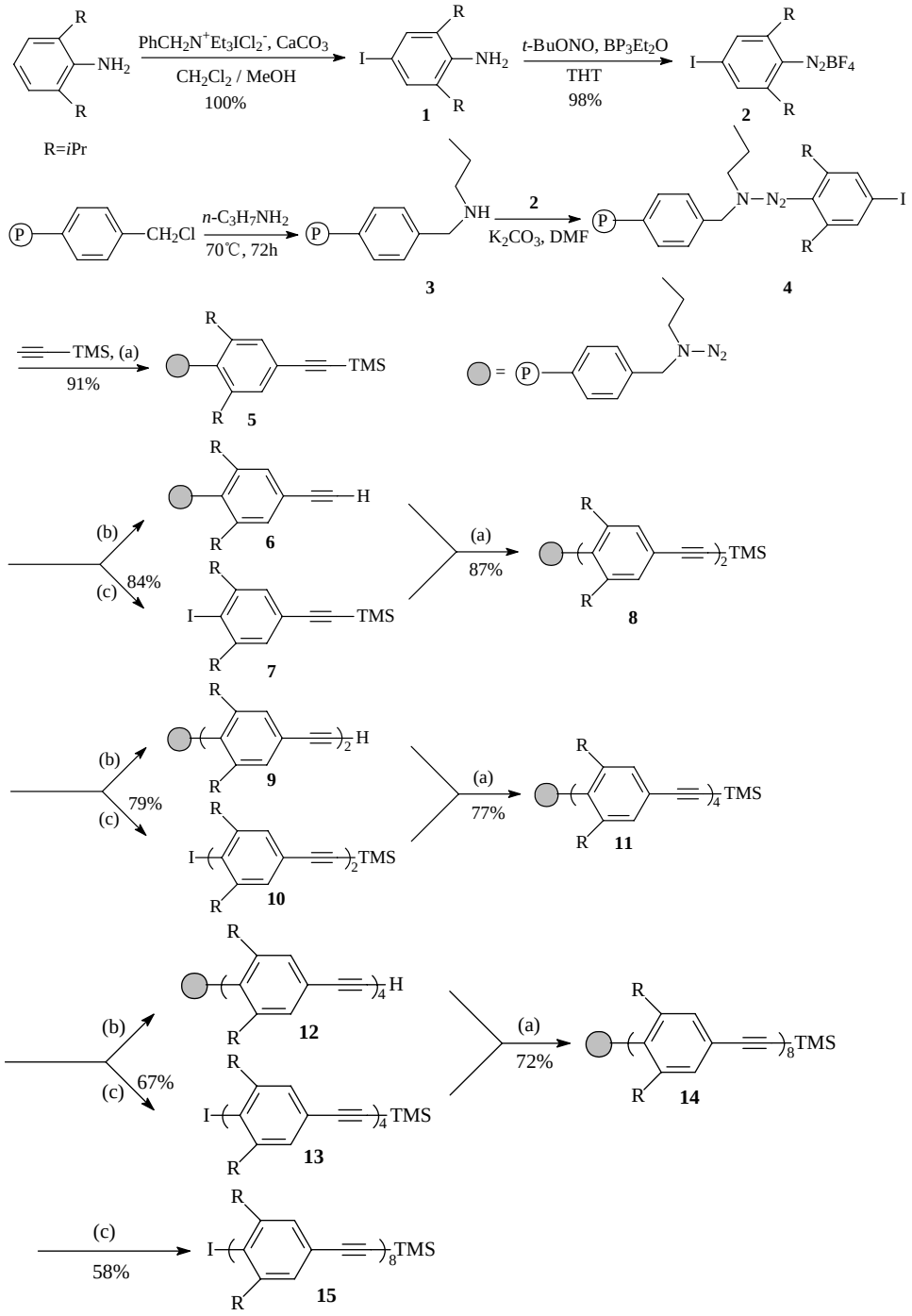
Keywords: Solid phase, monodisperse, oligo(1, 4-phenyleneethynylene)s.

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 for their excellent main-chain rigidity and interesting electronic characteristics such as negative differential resistance (NDR), bistable conductance states and controlled switching under an applied electric field[2-6]. Based on Tour's previous work, a facile route without any column chromatographic purifications was given here for the rapid synthesis of the soluble monodisperse oligo(1, 4-phenyleneethynylene)s up to ~60 Å by means of a solid phase iterative divergent/ convergent doubling strategy.

The synthetic route is outlined in **scheme 1**. Iodination of 2,6-diisopropylaniline was carried out with benzyltriethylammonium dichloroiodate to afford compound **1** in quantitive yield[7] which was then converted to the diazonium tetrafluoroborate salts **2** in high yield[8]. Merrifield's resin (chloromethylated polystyrene, 1% crosslinked with divinylbenzene, 200-400 mesh, 0.83 mequiv Cl/g, Sigma) 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 **2** 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 to give resin **5**, the desired starting monomer needed for the iterative divergent/convergent doubling strategy. One-third of **5** underwent desilylation by treatment with tetrabutylammonium fluoride(TBAF) in THF at room temperature to afford

* E-mail: xhwang@ciac.jl.cn

Scheme 1



Reagents: (a) $Pd(dba)_2$, CuI, PPh_3, Et_3N; (b) THF, TBAF; (c) MeI

the resin **6**. The remaining two-thirds of **5** was treated with MeI[5] at 115°C for 24 h to afford liberated monomer **7**. Resin **6** was then coupled with all of the liberated iodide **7** under Pd/Cu cross coupling conditions to afford the resin-supported dimer **8**. The sequence was repeated to generate the resin-supported tetramer **11** and finally octamer **14**. octamer **15** liberated from resin **14** by treatment with MeI at 115 °C for 12 h is about 60 Å and is quite soluble in common organic solvents such as THF, $CHCl_3$ and so on.

Because yield calculations for solid phase synthesis were quite difficult[5], the yields of solid phase reactions indicated in **Scheme 1** were thus only rough estimation based on the weight changes of the resin after each reaction. Compared with Tour's route, the starting monomer needed for the iterative divergent/convergent doubling strategy was simply synthesized through fewer easy-operation reaction steps, and the violent reagent *n*-BuLi was unnecessary. Most remarkably, time-consuming column chromatographic purifications were free throughout our synthesis, since compound **1** and all oligomers liberated from the resin were simply purified by passing through a silica gel plug and the obtained compound **2** was reasonably pure after precipitation from the reaction mixtures without any further purification. It was used directly for the next reaction. Our route is therefore obviously more facile, rapid and efficient.

Oligomers **7**, **10**, **13** and **15** were fully characterized by ^{1}H NMR, FTIR and MS. While compound **7**, **10** and **13** afforded molecular ion peak by direct laser desorption mass spectrometry, it was necessary to use matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) in order to obtain MS data on the octamer **15**. Using a dithranol matrix and in positive ion mode, we did obtain the desired M + 1 peak[10].

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10. Spectral data for oligomers: **7**. FTIR (KBr) 2962, 2870, 2158, 2068, 1550, 1467, 1362, 1331, 1249, 1183, 1101, 1065, 1000, 957, 759, 642 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz, δ ppm): 7.15 (s, 2H), 3.37 (septet, 2H, J = 6.8 Hz), 1.23 (d, 12H, J = 6.4Hz), 0.26 (s, 9H). LDI-MS:

384 (M^+). **10**. FTIR (KBr) 2961, 2869, 2154, 1546, 1462, 1417, 1383, 1362, 1248, 1168, 1105, 1070, 1000, 963, 942, 842, 758, 697 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz, δ ppm): 7.25 (s, 2H), 7.19 (s, 2H), 3.54 (septet, 2H, J = 6.8 Hz), 3.41 (septet, 2H, J = 3.6 Hz), 1.34-1.22 (m, 24H), 0.27 (s, 9H). LDI-MS: 568 (M^+), 441 (M – I). **13**. FTIR (KBr) 2960, 2868, 2153, 1594, 1546, 1463, 1417, 1383, 1362, 1247, 1168, 1106, 1071, 1000, 943, 880, 841, 731 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz, δ ppm): 7.25-7.13(m, 8H), 3.56-3.49 (m, 4H), 3.37-3.33 (m, 4H), 1.29-1.19 (m, 48H), 0.27 (s, 9H). LDI-MS: 937 (M^+), 865 (M-TMS), 810 (M–I). **15**. FTIR (KBr) 2960, 2868, 2151, 1595, 1546, 1463, 1418, 1383, 1362, 1247, 1168, 1105, 1071, 1000, 943, 880, 841, 767cm^{-1}. ^1H NMR ($CDCl_3$, 600MHz, δ ppm): 7.29-7.19(m, 16H), 3.62-3.55 (m, 8H), 3.49-3.38 (m, 8H), 1.36-1.20 (m, 96H), 0.26 (s, 9H). MALDI-MS: 1675 (M+H), 1602 (M-TMS), 1548 (M–I).

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