Stereocontrolled Synthesis of *cis*- and *trans*-Oligo(phenylene vinylene)s via Palladium-Catalyzed Cross-Coupling Reactions

Hiroyuki Katayama, *,[†] Masato Nagao,[†] Fumiyuki Ozawa,^{*, †} Masashi Ikegami,[‡] and Tatsuo Arai[‡] International Research Center for Elements Science, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan, and Department of Chemistry, Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan hiroyuki@scl.kyoto-u.ac.jp, ozawa@scl.kyoto-u.ac.jp

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General Experimental Methods. All manipulations using organometallic compounds were carried out under a nitrogen atmosphere using standard Schlenk-line techniques. ¹H and ¹³C NMR spectra were recorded at 300.11 and 75.46 MHz, respectively. Chemical shifts are reported in δ (ppm), referred to the ¹H (of residual protons) and ¹³C signals of deuterated solvents. Mass spectra were measured with a GCmass spectrometer (EI, 70 eV). GLC analysis was performed on an instrument equipped with an FID detector and CBP-1 capillary column (25 m × 0.25 mm). Recycle GPC (preparative) was performed with CHCl₃ as an eluent. Flash column chromatography was performed using silica gel 60 (230-400 mesh). The following compounds were synthesized according to literatures: 2,5-dioctyloxybenzeneboronic acid (1a),¹ 2,5-dioctyloxybenzene-1,4-diboronic acid (1b),² (Z)-styryl bromide (2a),³ (Z,Z)-1,4-bis(2bromoethenyl)benzene (**2b**),⁴ 2,5-dioctyloxyiodobenzene (**3a**),⁵ 2,5-dioctyloxy-1,4-diiodobenzene (**3b**),⁶ (Z)-dimethyl[3,5-bis(trifluoromethyl)phenyl]styrylsilane $(4a),^{7}$ (E, E)-1,4-bis[2-{dimethyl(3,5bis(trifluoromethyl)phenyl)silyl}ethenyl]benzene (**4b**),⁸ dimethyl[3,5-bis(trifluoromethyl)phenyl]silane,⁹ (*p*-bromophenyl)acetylene, ¹⁰ Pd(PPh₃)₄, ¹¹ [Pd(η^3 -allyl)(μ -Cl)]₂, ¹² and RuHCl(CO)(PPh₃)₃, ¹³ All other chemicals were obtained from commercial suppliers and used without further purification.

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 $^{13}C\{^{1}H\}$ NMR (CDCl₃, 75 MHz) of cis-OPV2





 $^{13}\mathrm{C}$ NMR (CDCl_3, 75 MHz) of $1\,c$





 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (CDCl₃, 75 MHz) of $2\,c$



¹H NMR (CDCl₃, 300 MHz) of *cis*-**OPV3**



 $^{13}C\{^{1}H\}$ NMR (CDCl₃, 75 MHz) of cis-OPV3



¹H NMR (CDCl₃, 300 MHz) of *cis*-**OPV4**



¹³C{¹H} NMR (CDCl₃, 75 MHz) of *cis*-OPV4





¹H NMR (CDCl₃, 300 MHz) of trans-OPV2



S9



¹³C{¹H} NMR (CDCl₃, 75 MHz) of $\mathbf{6}$











 $^{13}C\{^{1}H\}$ NMR (CDCl₃, 75 MHz) of ${\bf 8}$







 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (CDCl₃, 75 MHz) of $4\,c$





 $^{13}\text{C}\{^{1}\text{H}\}$ NMR (CDCl₃, 75 MHz) of $3\,c$



¹H NMR (CDCl₃, 300 MHz) of *trans*-**OPV3**



¹³C{¹H} NMR (CDCl₃, 75 MHz) of *trans*-**OPV3**



¹H NMR (CDCl₃, 300 MHz) of trans-OPV4



 $^{13}C\{^{1}H\}$ NMR (CDCl₃, 75 MHz) of trans-**OPV4**







¹H NMR (CDCl₃, 300 MHz) of **OPV4** before (top) and after (bottom) photoisomerization

