Supporting Information

A Phenylene-alkylated Thiophene-based partially Ladder-type Conjugated Polymer

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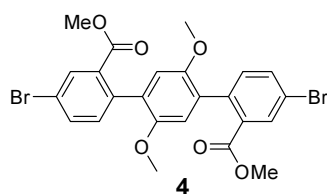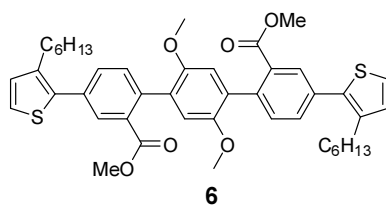*[*]E-mail: tkim@incheon.ac.kr*

Experimental

Melting points were determined using Büchi 510 melting point apparatus and uncorrected. IR spectra were recorded on a Nicolet MAGNA 560-FTIR spectrometer. ^{1}H NMR spectra were recorded on a Bruker Advance DPX-300, Bruker Advance DPX-500 instruments and Agilent 400-MR (400 MHz) instrument using d_6-DMSO or $CDCl_3$ as a reference or internal deuterium lock. The chemical shift data for each signal are given in units of d (ppm) relative to tetramethylsilane (TMS) where d (TMS) = 0, and referenced to the solvent residual. ^{13}C NMR spectra were recorded on a Bruker Advance-300 (75.4 MHz) instrument and Agilent 400-MR (100MHz) instrument using internal deuterium lock and proton decoupling. Mass spectra were obtained on a JEOL JMS-AX505WA instrument. Thermal stability of the polymer was analyzed by the thermogravimetric analysis measurements on a Shimadzu TGA-2950 instrument at a heating rate of 10 °C min^{-1} in a nitrogen flow. The glass transition temperature (T_g) was measured using a Perkin-Elmer Pyris-1 DSC from 20 °C to 310 °C with a scan rate of 10 °C min^{-1} under nitrogen. UV-visible absorption spectra and fluorescence spectra were measured with Hewlett Packard 8452A diode array spectrometer and SPEX Fluorolog-t2 fluorometer (model FL 112, 450 W, xenon lamp), respectively, using spectral grade $CHCl_3$ as a solvent. The measurements were carried out at 25 °C using a quartz cell with a path length of 1 cm. All electrochemical measurements were made with a COMPACTSTAT potentiostat (IVIUM Technologies) using an Pt wire reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) in anhydrous CH_3CN. Typical cyclic voltammograms were recorded using ITO electrodes as the working electrode and a platinum coil counter electrode. The ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was used as an external reference. The potential values were converted to versus Ag/AgCl. Molar masses were determined by Gel Permeation Chromatography (GPC) using two PL Gel 30 cm 5 μm mixed C columns at 30 °C running in THF and calibrated against polystyrene (M_n = 600-10^6 g/mol) standards using a Knauer refractive index detector. The X-ray diffraction patterns of the oligomer thin film were recorded using a Philips XPERT-PRO MRD diffractometer by employing a scanning range (2θ) from 1° to 30° with a Cu Kα1 X-ray (λ =1.540598 Å).
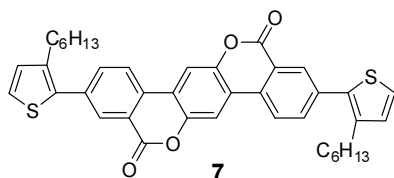
Reagents were purified and dried by standard technique. All air and water-sensitive synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques.

Synthesis of the Diester Diketone 4. Bromo iodoester **2** (1.21 g, 3.54 mmol), dimethoxy diboronic ester **3** (0.4 g, 1.77 mmol) were added in a mixture of aqueous Na$_2$CO$_3$ (2.0 M; 3.54 mL) and toluene (13 mL) were taken together in a Schlenk flask and purged with nitrogen for 30 min. To this tetrakis(triphenylphosphine)palladium (0.02 mg, 0.12 mmol) was added and the reaction mixture was heated at 75 °C under nitrogen for 2 days to produce a black suspension. The reaction mixture was cooled to room temperature and water (20 mL) was added. The mixture was extracted with dichloromethane (3 × 50 mL) and the combined organic layers were washed with HCl (1 M; 50 mL), water (50 mL), brine (50 mL), dried over MgSO$_4$ and evaporated under reduced pressure. The crude product was recrystallized from EtOAc to give the product **4** as a white crystal (0.92 g, 52%); mp 223-224 °C; R$_f$ 0.24 (10:1 hexane:EtOAc); ν$_{max}$(CHCl$_3$)/ cm^{-1} 3020, 2925, 1711, 1670, 1421, 1362, 1215 and 669; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.02 (2H, s, 2×ArH), 7.96 (2H, d, J = 8.2 2×ArH), 7.30 (2H, d, J = 8.2, 2×ArH), 6.79 (2H, s, 2×ArH), 3.73 (6H, s, 2×COOCH_3), 3.69 (6H, s, 2×OCH_3); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 167.2, 150.1, 137.2, 134.4, 133.4, 132.8, 132.4, 129.3, 121.2, 112.6, 55.9 and 52; m/z (FAB+) 562 [M$^+$, 50%], 564 (27%) and 563 [(M+H)$^+$, 14%]; [Found: M$^+$ 561.9627. C$_{24}$H$_{20}$Br$_2$O$_6$ requires M, 561.9627].

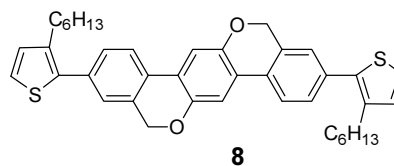2 *Bull. Korean Chem. Soc.* **2013**, Vol. 34, No. 8

Notes

Synthesis of the Compound 6: Dibromo diester **4** (0.4 g, 0.71 mmol), hexyl thiophenyl boronic ester **5** (0.42 g, 1.42 mmol), and aqueous K_3PO_4 (2.0 M; 1.42 mL) were added in 6.5 mL of toluene in a Schlenk flask, and purged with nitrogen for 30 min. To this tetrakis (triphenylphosphine) palladium (0.06 g, 0.04 mmol) was added and the reaction mixture was heated at 110 ℃ under nitrogen for 2 days to produce a black suspension. The reaction mixture was cooled to room temperature and water (10 mL) was added. The mixture was extracted with dichloromethane (3 × 30 mL) and the combined organic layers were washed with HCl (1 M; 20 mL), water (20 mL), brine (20 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography(10:1 hexane:EtOAc) to give the product **6** as a pale yellow oil; R_f 0.33 (10:1 hexane:EtOAc); ν_{max} (CHCl$_3$)/cm^{-1} 3020, 2928, 1710, 1602, 1421, 1362, 1205 and 669; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.01 (2H, s, 2×Ar*H*), 7.6 (2H, d, *J* = 8.0, 2×Ar*H*), 7.42 (2H, d, *J* = 8.0, 2×Ar*H*), 7.2 (2H, d, *J* = 5.0, 2×Ar*H*), 6.9 (2H, d, *J* = 5.0, 2×Ar*H*), 6.79 (2H, s, 2×Ar*H*), 3.66 (6H, s, 2×COOC*H*$_3$), 3.65 (6H, s, 2×OC*H*$_3$), 2.64 (4H, t, *J* = 7.0, 2×ArC*H*$_2$), 1.61 (4H, m, 2×ArCH$_2$C*H*$_2$), 1.25 (12H, m, 2×Ar(CH$_2$)$_2$(C*H*$_2$)$_3$), 0.86(6H, t, *J* = 7.5, 2×Ar(CH$_2$)$_5$C*H*$_3$); ^{13}C NMR (75.4 MHz CDCl$_3$) δ 168.5, 150.3, 139.4, 137.1, 136.4, 132.1, 131.5, 130.2, 129.6, 124.2, 112.8, 55.9, 51.8, 31.7, 31, 29.7, 28.7, 22.6 and 14.1; *m/z* (FAB+) 738 [M$^+$, 100%], 739 [(M+H)$^+$, 51%] and 740 (27%); [Found: M$^+$ 738.3049. $C_{44}H_{50}O_6S_2$ requires *M*, 738.3049].
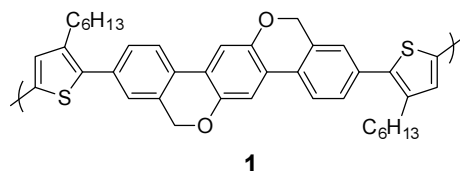

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Cyclization of the Compound 6 to Give 7. To a solution of the non-cyclized precursor **6** (0.25 g, 0.31 mmol) in dichloromethane (4 mL), BBr$_3$ (1.25 mL of 1.0 M in dichloromethane, 1.25 mmol) was added at room temperature under nitrogen. The reaction mixture was further left to stir for 10 min at room temperature, followed by the addition of water (5 mL). The solution was extracted dichloromethane (3 × 30 mL) and dried over MgSO$_4$ and evaporated under reduced pressure. The crude product was recrystallized from EtOAc to give the cyclized product **7** as a bright yellow crystal (0.18 g, 89%); mp 178-180 ℃; R_f 0.37 (10:1 hexane:EtOAc); ν_{max} (CHCl$_3$)/cm^{-1} 3066, 2930, 1710, 1521, 1423, 1362, 1217 and 656; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.53 (2H, s, 2×Ar*H*), 8.16 (2H, d, *J* = 8.5 2×Ar*H*), 8.05 (2H, s, 2×Ar*H*), 7.96 (2H, d, *J* = 8.5, 2×Ar*H*), 7.33 (2H, d, *J* = 5.5, 2×Ar*H*), 7.05 (2H, d, *J* = 5.5, 2×Ar*H*), 2.74 (4H, t, *J* = 7.5, 2×ArC*H*$_2$), 1.61 (4H, m, 2×ArCH$_2$C*H*$_2$), 1.21 (12H, m, 2×Ar(CH$_2$)$_2$(C*H*$_2$)$_3$), 0.88 (6H, t, *J* = 6.5, 2×Ar(CH$_2$)$_5$C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 160.3, 140.4, 140, 135.7, 135.3, 131.8, 130.6, 130.1, 125.2, 122.6, 119.8, 111.1, 31.6, 30.9, 29.7, 29.2, 28.9, 22.6 and 14.1; *m/z* (FAB+) 647 [(M+H)$^+$, 100%], 648 (46%) and 649 (20%); [Found:

(M+H)$^+$, 647.2290. $C_{44}H_{39}O_4S_2$ requires *M*, 647.2290].

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Reduction of the Diester 7 to Give 8. To a cooled solution of compound **7** (0.43 g, 0.67 mmol) in a mixture of boron trifluoride etherate(17 mL) and tetrahydrofuran (23 mL) was added over 15 min to a suspension of sodium borohydride (0.53 g, 13.89 mmol) in tetrahydrofuran(20 mL) under nitrogen while maintaining the reaction temperature below 10 ℃. The reaction mixture was then raised within 30 min to the reflux temperature, kept under reflux for 1 h, and then cooled to −3 ℃. Ice cold aqueous hydrochloric acid (2.0 M; 24 mL) was then cautiously added and the temperature was allowed to increase to room temperature. Water (100 mL) was added and the reaction mixture was extracted with chloroform (3 × 30 mL). The combined extracts were evaporated and the oily residue was heated at 80℃ with aqueous sodium hydroxide solution (2.0 M; 24 mL) for 20 min. The resulting mixture was cooled and extracted with ether (3 × 30 mL). The ether extracts were combined, dried over sodium sulfate, and evaporated. The crude product was purified by column chromatography (30:1 hexane:EtOAc) to give the product **8** as a pale yellow crystal (0.25 g, 60%); mp 193-195 ℃ R_f 0.3 (30:1 hexane:EtOAc); ν_{max} (CHCl$_3$)/cm^{-1} 3019, 2916, 1517, 1479, 1422, 1362, 1291, 1215 and 668; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.62 (2H, d, *J* = 8.0, 2×Ar*H*), 7.34 (2H, d, *J* = 8.0 2×Ar*H*), 7.27 (2H, s, 2×Ar*H*), 7.14-7.13 (4H, m, 4×Ar*H*), 6.89 (2H, d, *J* = 5.0, 2×Ar*H*), 5.04 (4H, s, 2×ArC*H*$_2$), 2.6 (4H, t, *J* = 7.5, 2×ArC*H*$_2$), 1.53-1.5 (4H, m, 2×ArCH$_2$C*H*$_2$), 1.17 (12H, m, 2×Ar(CH$_2$)$_2$(C*H*$_2$)$_3$), 0.76 (6H, t, *J* = 6.5, 2×Ar(CH$_2$)$_5$C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 149.9, 139.1, 137.1, 134.6, 131.9, 129.7, 129.4, 128.8, 125.5, 123.9, 123.7, 122.4, 111.5, 68.6, 31.7, 30.9, 30.4, 29.8, 29.2, 28.8, 22.6 and 14.1; *m/z* (FAB+) 618 [M$^+$, 100%], 619 [(M+H)$^+$,46%] and 620(20%); [Found: M$^+$ 618.2626. $C_{40}H_{42}O_2S_2$ requires *M*, 618.2626].

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Synthesis of the Polymer 1. The monomer **8** (0.28 g, 0.36 mmol) was dissolved in dry chloroform (7 mL), and this solution was added dropwise to a suspention of FeCl$_3$ (0.24 g, 1.49 mmol) in dry chloroform (20 mL) at 0 ℃ for 30 min. The mixture was vigorously stirred for 6 h at 0 ℃ and then at room temperature for 19 h under nitrogen. The polymer was precipitated into methanol (300 mL) and purified by Soxhlet extraction with methanol, hexane, acetone and

toluene. Further precipitation into methanol was carried out to give the desired polymer **1** (0.12 g, 42%) as a yellow powder; ν_{max}(CHCl$_3$)/cm^{-1} 3123, 1521, 1422, 1362, 1214, 928 and 670; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.66 (2H, br sgnal, 2×Ar*H*), 7.4-7.38 (6H, m, 2×Ar*H$_3$*), 7.02 (2H, m, 2×Ar*H*), 5.1 (4H, br s, 2×ArC*H$_2$*), 2.62 (4H, m, 2×ArC*H$_2$*), 1.56 (4H, m, 2×ArCH$_2$C*H$_2$*) 1.19 (12H, m, 2×Ar(CH$_2$)$_2$-(C*H$_2$)$_3$*), 0.81-0.79 (6H, m, 2×Ar(CH$_2$)$_5$C*H$_3$*)); GPC (THF, RI)/Da M_n 8.9 × 10^3. M_w 25.2 × 10^3 and M_w/M_n 2.8.

Figure S1. Packing diagrams of **8**.

Figure S2. Molecular Structure of **8**.

Table S1. Crystal data and structure refinement for icu1

Identification code	icu1
Empirical formula	C20 H21 O S
Formula weight	309.43
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimension	α = 105.9110(10)°.
a = 5.45160(10) Å	
b = 9.9064(2) Å	β = 98.7710(10)°.
c = 15.7585(3) Å	γ = 92.5810(10)°.
Volume	805.49(3) Å3
Z	2
Density (calculated)	1.276 Mg/m^3
Absorption coefficient	0.201 mm^{-1}
F(000)	330
Crystal size	0.29 × 0.20 × 0.08 mm^3
Theta range for data collection	2.15 to 26.98°.
Index ranges	-6≤h≤6, -12≤k≤12, -20≤l≤20
Reflections collected	13954
Independent reflections	3498 [R(int) = 0.0266]
Completeness to theta = 26.98°	99.9%
Absorption correction	None
Max. and min. transmission	0.9851 and 0.9434
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3498 / 0 / 199
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0974
R indices (all data)	R1 = 0.0458, wR2 = 0.1034
Largest diff. peak and hole	0.271 and -0.259 e.Å^{-3}

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for icu1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

X	y	z	U(eq)	
S(1)	7944(1)	-836(1)	1649(1)	33(1)
O(1)	-3738(2)	3788(1)	-1432(1)	28(1)
C(1)	-5852(3)	4592(1)	-1486(1)	26(1)
C(2)	-1922(3)	4416(1)	-700(1)	24(1)
C(3)	-653(3)	3554(1)	-266(1)	25(1)
C(4)	1312(3)	4119(1)	446(1)	24(1)
C(5)	2805(3)	3274(1)	929(1)	24(1)
C(6)	2119(3)	1873(2)	878(1)	27(1)
C(7)	3704(3)	1125(2)	1310(1)	29(1)
C(8)	6043(3)	1736(1)	1799(1)	26(1)
C(9)	6694(3)	3147(2)	1862(1)	26(1)
C(10)	5101(3)	3907(1)	1443(1)	24(1)
C(11)	7800(3)	916(1)	2215(1)	27(1)
C(12)	9526(3)	1324(2)	2990(1)	28(1)
C(13)	10964(3)	204(2)	3105(1)	34(1)
C(14)	10328(3)	-1009(2)	2439(1)	37(1)
C(15)	9956(3)	2772(2)	3649(1)	31(1)
C(16)	12186(3)	3660(2)	3529(1)	32(1)
C(17)	12307(3)	5207(2)	4048(1)	34(1)
C(18)	14350(3)	6112(2)	3854(1)	37(1)
C(19)	14513(3)	7662(2)	4355(1)	40(1)
C(20)	16541(4)	8534(2)	4128(2)	52(1)

Table S3. Bond lengths [Å] and angles [°] for icu1

S(1)-C(14)	1.7065(17)
S(1)-C(11)	1.7317(14)
O(1)-C(2)	1.3786(17)
O(1)-C(1)	1.4351(16)
C(1)-C(10)#1	1.5043(18)
C(2)-C(3)	1.380(2)
C(2)-C(4)#1	1.4054(19)
C(3)-C(4)	1.398(2)
C(4)-C(2)#1	1.4055(19)
C(4)-C(5)	1.4712(19)
C(5)-C(6)	1.3982(19)
C(5)-C(10)	1.399(2)
C(6)-C(7)	1.384(2)
C(7)-C(8)	1.400(2)
C(8)-C(9)	1.3993(19)
C(8)-C(11)	1.476(2)
C(9)-C(10)	1.3829(19)
C(10)-C(1)#1	1.5044(18)
C(11)-C(12)	1.373(2)
C(12)-C(13)	1.423(2)
C(12)-C(15)	1.506(2)
C(13)-C(14)	1.352(2)
C(15)-C(16)	1.533(2)
C(16)-C(17)	1.520(2)
C(17)-C(18)	1.517(2)
C(18)-C(19)	1.514(2)
C(19)-C(20)	1.517(3)
C(14)-S(1)-C(11)	92.04(7)
C(2)-O(1)-C(1)	112.85(10)
O(1)-C(1)-C(10)#1	111.97(11)
O(1)-C(2)-C(3)	117.89(12)
O(1)-C(2)-C(4)#1	120.20(12)
C(3)-C(2)-C(4)#1	121.81(13)
C(2)-C(3)-C(4)	120.62(12)
C(3)-C(4)-C(2)#1	117.57(13)
C(3)-C(4)-C(5)	124.15(12)
C(2)#1-C(4)-C(5)	118.27(13)
C(6)-C(5)-C(10)	118.42(13)
C(6)-C(5)-C(4)	124.26(13)
C(10)-C(5)-C(4)	117.27(12)
C(7)-C(6)-C(5)	120.59(14)
C(6)-C(7)-C(8)	121.26(13)
C(9)-C(8)-C(7)	117.78(13)
C(9)-C(8)-C(11)	120.76(13)
C(7)-C(8)-C(11)	121.44(13)
C(10)-C(9)-C(8)	121.21(13)
C(9)-C(10)-C(5)	120.67(13)
C(9)-C(10)-C(1)#1	120.90(13)
C(5)-C(10)-C(1)#1	118.34(12)
C(12)-C(11)-C(8)	130.58(13)
C(12)-C(11)-S(1)	110.98(11)
C(8)-C(11)-S(1)	118.35(11)
C(11)-C(12)-C(13)	111.73(13)
C(11)-C(12)-C(15)	126.01(13)
C(13)-C(12)-C(15)	122.25(14)
C(14)-C(13)-C(12)	113.66(15)
C(13)-C(14)-S(1)	111.59(12)
C(12)-C(15)-C(16)	112.95(13)
C(17)-C(16)-C(15)	113.27(13)

Table S3. Bond lengths [Å] and angles [°] for icu1

C(18)-C(17)-C(16)	113.23(13)
C(19)-C(18)-C(17)	114.60(14)
C(18)-C(19)-C(20)	112.98(15)

Symmetry transformations used to generate equivalent atoms: #1 −x, −y+1, −z

Table S4. Anisotropic displacement parameters (Å2 × 10³) for icu1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	39(1)	21(1)	38(1)	7(1)	5(1)	4(1)
O(1)	27(1)	21(1)	31(1)	3(1)	1(1)	3(1)
C(1)	24(1)	23(1)	31(1)	8(1)	5(1)	2(1)
C(2)	23(1)	23(1)	25(1)	3(1)	7(1)	2(1)
C(3)	27(1)	18(1)	31(1)	5(1)	9(1)	1(1)
C(4)	24(1)	21(1)	26(1)	6(1)	9(1)	3(1)
C(5)	26(1)	21(1)	26(1)	6(1)	9(1)	4(1)
C(6)	27(1)	24(1)	30(1)	6(1)	5(1)	0(1)
C(7)	32(1)	22(1)	33(1)	8(1)	8(1)	0(1)
C(8)	29(1)	23(1)	29(1)	8(1)	10(1)	4(1)
C(9)	24(1)	26(1)	29(1)	7(1)	6(1)	2(1)
C(10)	26(1)	20(1)	26(1)	5(1)	10(1)	2(1)
C(11)	30(1)	22(1)	32(1)	8(1)	10(1)	3(1)
C(12)	29(1)	26(1)	32(1)	10(1)	8(1)	3(1)
C(13)	36(1)	32(1)	38(1)	16(1)	5(1)	6(1)
C(14)	41(1)	28(1)	46(1)	17(1)	9(1)	10(1)
C(15)	33(1)	31(1)	29(1)	7(1)	6(1)	5(1)
C(16)	31(1)	31(1)	34(1)	6(1)	7(1)	5(1)
C(17)	34(1)	31(1)	36(1)	5(1)	8(1)	3(1)
C(18)	36(1)	33(1)	40(1)	7(1)	10(1)	3(1)
C(19)	41(1)	32(1)	45(1)	9(1)	10(1)	1(1)
C(20)	49(1)	40(1)	70(1)	17(1)	14(1)	-2(1)

Table S5. Hydrogen coordinates (× 10⁴) and isotropic displacement parameters (Å2 × 10³) for icu1

	x	y	z	U(eq)
H(1A)	-6751	4584	-987	31
H(1B)	-7005	4145	-2055	31
H(3A)	-1120	2568	-452	30
H(6A)	550	1431	544	33
H(7A)	3196	178	1275	35
H(9A)	8258	3591	2198	32
H(13A)	12251	300	3604	41
H(14A)	11111	-1854	2413	44
H(15A)	10239	2676	4265	38
H(15B)	8439	3271	3578	38
H(16A)	13742	3272	3729	39
H(16B)	12088	3581	2885	39
H(17A)	10683	5569	3897	41
H(17B)	12588	5294	4697	41
H(18A)	15970	5747	4006	44
H(18B)	14071	6013	3203	44
H(19A)	14837	7769	5007	48
H(19B)	12889	8029	4212	48
H(20A)	16562	9524	4471	78
H(20B)	16210	8452	3486	78
H(20C)	18160	8191	4281	78

Notes

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