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Structural effects of dibromocarbazoles on direct arylation polycondensation with 3,4-ethylenedioxythiophene

Wei Li and Tsuyoshi Michinobu*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

*Correspondence Address:

Assoc. Prof. Tsuyoshi Michinobu

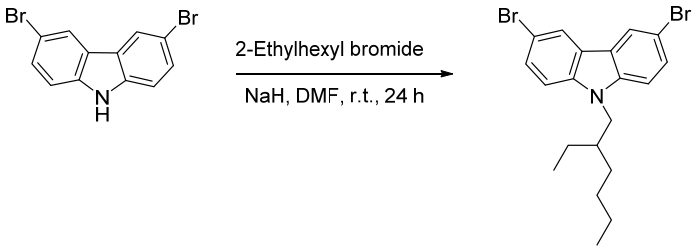
Department of Organic and Polymeric Materials, Tokyo Institute of Technology

2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Tel/Fax: +81-3-5734-3774, E-mail: michinobu.t.aa@m.titech.ac.jp

1. Synthesis

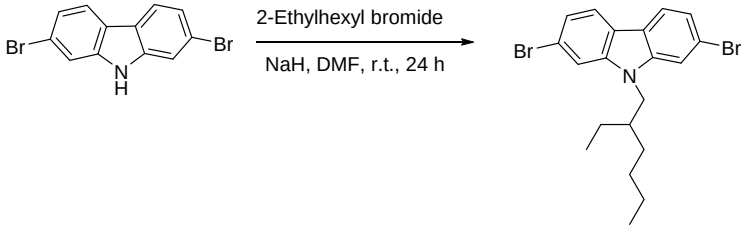
1.1. Synthesis of 3,6-dibromo-9-(2-ethylhexyl) carbazole (1)[S1]



1

A solution of 3,6-dibromocarbazole (1.00 g, 3.10 mmol) and NaH (0.20 g, 4.5 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min. 2-Ethylhexyl bromide (0.90 g, 4.5 mmol) was added by a syringe. The mixture was stirred at room temperature for 24 h. Water was added, and the organic layer was extracted with CH_2Cl_2 (30 mL x 3). After the combined organic layers were dried over $MgSO_4$, the solvent was removed under reduced pressure. Column chromatography (SiO_2, hexane) gave the desired product as colorless liquid (1.00 g, 75%). ^{1}H NMR (300 MHz, $CDCL_3$): δ 8.08 (d, *J* = 1.7 Hz, 2H), 7.53 (dd, *J* = 1.8, 8.7 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 4.02 (d, *J* = 7.5 Hz, 2H), 2.15–1.83 (m, 1H), 1.41–1.08 (m, 8H), 1.00–0.69 ppm (m, 6H). ^{13}C NMR (75 MHz, $CDCL_3$): δ 140.49, 129.72, 124.12, 123.93, 112.64, 111.38, 48.23, 39.93, 31.54, 29.35, 24.93, 23.61, 14.61, 11.46 ppm. IR (neat): ν = 2958, 2928, 2869, 1847, 1719, 1622, 1588, 1548, 1470, 1437, 1380, 1363, 1343, 1285, 1147, 1057, 1018, 965, 911, 867, 834, 795, 742, 713, 665, 644, 614 cm^{-1}.

1.2. Synthesis of 2,7-dibromo-9-(2-ethylhexyl)carbazole (2)[S2]

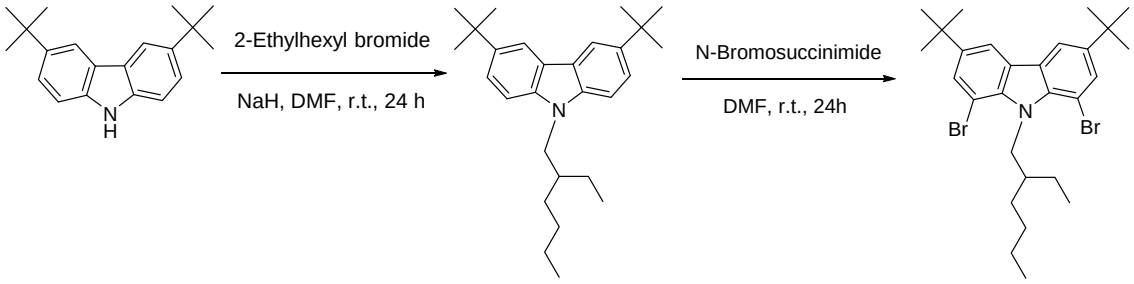


2

A solution of 2,7-dibromocarbazole (1.00 g, 3.10 mmol) and NaH (0.2 g, 4.5 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min. 2-Ethylhexyl bromide (0.90 g, 4.5 mmol) was added by a syringe. The mixture was stirred at room temperature for 24 h. Water was added, and the organic layer was extracted with CH_2Cl_2 (30 mL x 3). After the combined organic layers were dried over $MgSO_4$, the solvent was removed under reduced pressure. Column chromatography (SiO_2, hexane) gave the desired product as colorless liquid (1.1 g, 82%). ^{1}H NMR (300 MHz, $CDCL_3$): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 1.1 Hz, 2H), 7.33 (dd, *J* = 1.4, 8.3 Hz, 2H), 4.00 (dd, *J* = 2.7, 7.5 Hz, 2H), 2.33–1.70 (m, 1H), 1.45–1.15 (m, 8H), 1.02–0.82 ppm (m, 6H). ^{13}C NMR (75 MHz, $CDCL_3$): δ 142.70, 123.35, 122.26, 122.07, 120.49, 113.12, 48.39, 39.84, 31.46, 29.23, 25.00, 23.72, 14.70, 11.56 ppm. IR (neat): ν = 2958, 2925, 2859, 1859, 1682, 1620,

1584, 1482, 1451, 1327, 1310, 1225, 1247, 1131, 1054, 997, 967, 946, 910, 876, 843, 820, 796, 767, 743, 701, 685, 666, 651, 638 cm^{-1}.

1.3. Synthesis of 1,8-dibromo-3,6-di-*tert*-butyl-9-(2-ethylhexyl)carbazole (3)

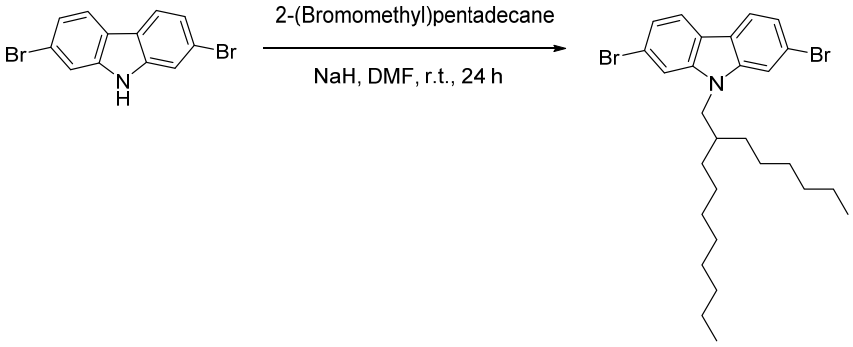


3

A solution of 3,6-di-*tert*-butylcarbazole[S3] (0.725 g, 2.56 mmol) and NaH (0.160 g, 4.00 mmol) in DMF (6 mL) was degassed with nitrogen for 15 min. 2-Ethylhexyl bromide (0.772 g, 4.00 mmol) was added by a syringe. After the mixture was stirred at room temperature for 24 h, water was added. The organic layer was extracted with CH_2Cl_2 (30 mL x 3). Combined organic solutions were dried over $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (SiO_2, hexane) gave 3,6-di-*tert*-butyl-9-(2-ethylhexyl)carbazole as light yellow liquid (0.940 g, 92%). ^{1}H NMR (300 MHz, $CDCL_3$): δ 8.05 (d, *J* = 1.6 Hz, 2H), 7.45 (dd, *J* = 1.8, 8.6 Hz, 2H), 7.22 (d, *J* = 6.0 Hz, 2H), 4.05 (dd, *J* = 4.6, 7.2 Hz, 2H), 2.01 (s, 1H), 1.42 (s, 18H), 1.33–1.17 (m, 8H), 0.85 ppm (d, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCL_3$): δ 141.62, 139.79, 123.41, 122.84, 116.38, 108.50, 47.66, 39.69, 34.74, 32.16, 31.93, 31.69, 31.12, 29.02, 24.50, 23.19, 22.74, 14.19, 14.16, 10.97 ppm. IR (neat): ν = 2956, 2928, 2868, 1674, 1602, 1486, 1465, 1381, 1324, 1293, 1255, 1219, 1158, 1124, 1058, 1023, 913, 802, 744, 657, 634 cm^{-1}. MADLI-TOF (M_w = 391.6): m/z = 392.8 ([M+H^+]).

A solution of 3,6-di-*tert*-butyl-9-(2-ethylhexyl)carbazole (0.940 g, 2.40 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min. To this solution, *N*-bromosuccinimide (1.068 g, 6.000 mmol) in DMF (3 mL) was added by a syringe at 5 ^{o}C. After the mixture was stirred at room temperature for 24 h, CH_2Cl_2, was added. The organic layer was washed with water and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by column chromatography (SiO_2, hexane) gave the desired product as light yellow liquid (1.020 g, 73%). ^{1}H NMR (300 MHz, $CDCL_3$): δ 8.00 (d, *J* = 1.5 Hz, 2H), 7.66 (d, *J* = 1.6 Hz, 2H), 5.16 (d, *J* = 7.8 Hz, 2H), 2.05–1.85 (m, 1H), 1.45 (s, 18H), 1.04 (m, 8H), 0.75 ppm (dd, *J* = 3.1, 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCL_3$): δ 145.45, 138.65, 131.25, 127.56, 116.34, 105.40, 49.07, 40.98, 35.51, 32.70, 30.02, 28.66, 23.92, 23.57, 14.75, 11.59 ppm. IR (neat): ν = 2957, 2929, 2866, 1747, 1603, 1547, 1481, 1464, 1420, 1383, 1363, 1300, 1284, 1263, 1246, 1203, 1182, 1122, 1058, 908, 867, 838, 791, 733, 665, 639 cm^{-1}. MADLI-TOF (M_w = 549.4): m/z = 550.9 ([M+H^+]).

1.4. Synthesis of 2,7-dibromo-9-(2-hexyldecyl)carbazole (4)



4

A solution of 2,7-dibromocarbazole (0.488 g, 1.50 mmol) and NaH (0.1 g, 2.5 mmol) in DMF (4 mL) was degassed with nitrogen for 15 min. 7-(Bromomethyl)pentadecane (0.76 g, 2.5 mmol) was added by a syringe. The mixture was stirred at room temperature for 24 h. Water was added, and the organic layer was extracted with CH_2Cl_2 (30 mL x 3). After the combined organic layers were dried over $MgSO_4$, the solvent was removed under reduced pressure. Column chromatography (SiO_2, hexane) gave the desired product as colorless liquid (0.70 g, 85%). ^{1}H NMR (300 MHz, $CDCL_3$): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 1.4 Hz, 2H), 7.33 (dd, *J* = 8.1, 1.3 Hz, 2H), 4.01 (d, *J* = 7.5 Hz, 2H), 2.06 (s, 1H), 1.25 (d, *J* = 16.9 Hz, 24H), 0.94–0.80 ppm (m, 6H). ^{13}C NMR (75 MHz, $CDCL_3$): δ 142.58, 123.24, 122.14, 121.96, 120.39, 113.02, 48.45, 40.41, 40.13, 38.19, 33.20, 32.54, 32.50, 32.41, 32.26, 30.53, 30.22, 30.13, 29.90, 26.99, 23.29, 14.71. IR (neat): ν = 2955, 2923, 2870, 2852, 1485, 1457, 1441, 1415, 1375, 1339, 1319, 1249, 1199, 1145, 1071, 996, 962, 911, 860, 826, 813, 794, 740, 723, 709, 695, 652, 632, 616 cm^{-1}.

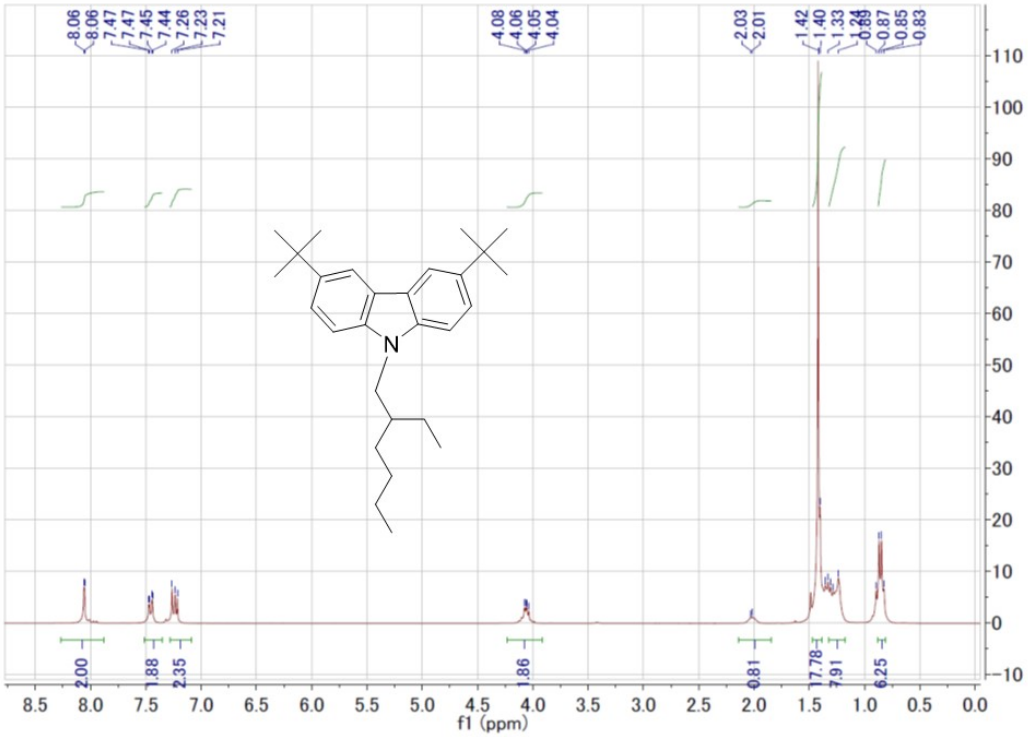


Fig. S1 ^{1}H-NMR spectrum of 3,6-di-*tert*-butyl-9-(2-ethylhexyl)carbazole in $CDCl_3$.

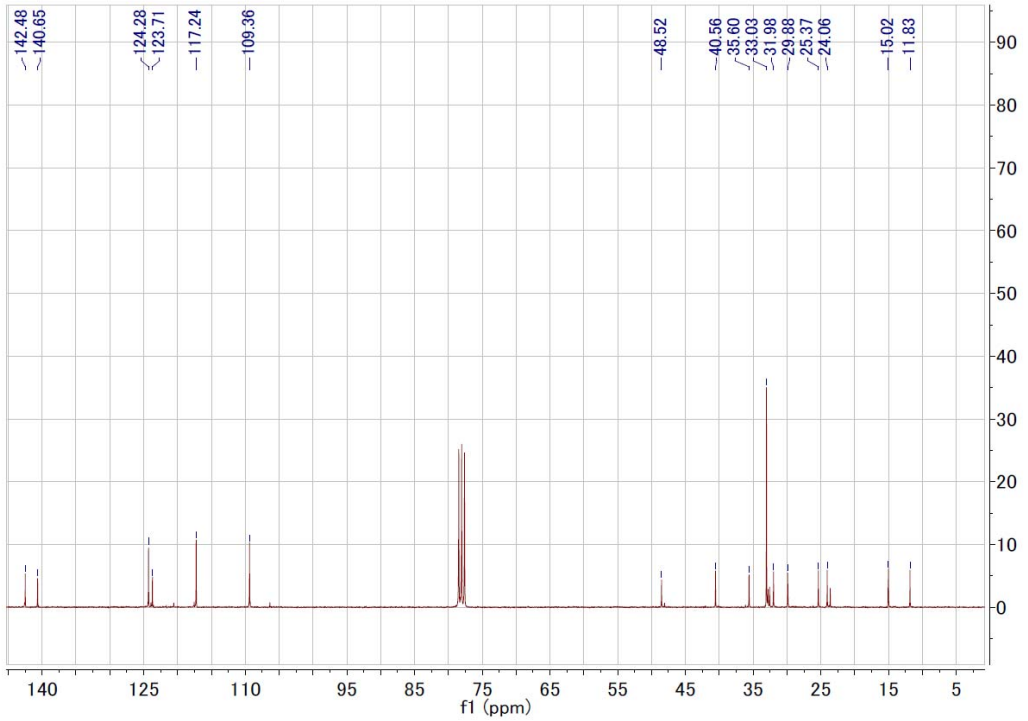


Fig. S2 ^{13}C-NMR spectrum of 3,6-di-*tert*-butyl-9-(2-ethylhexyl)carbazole in $CDCl_3$.

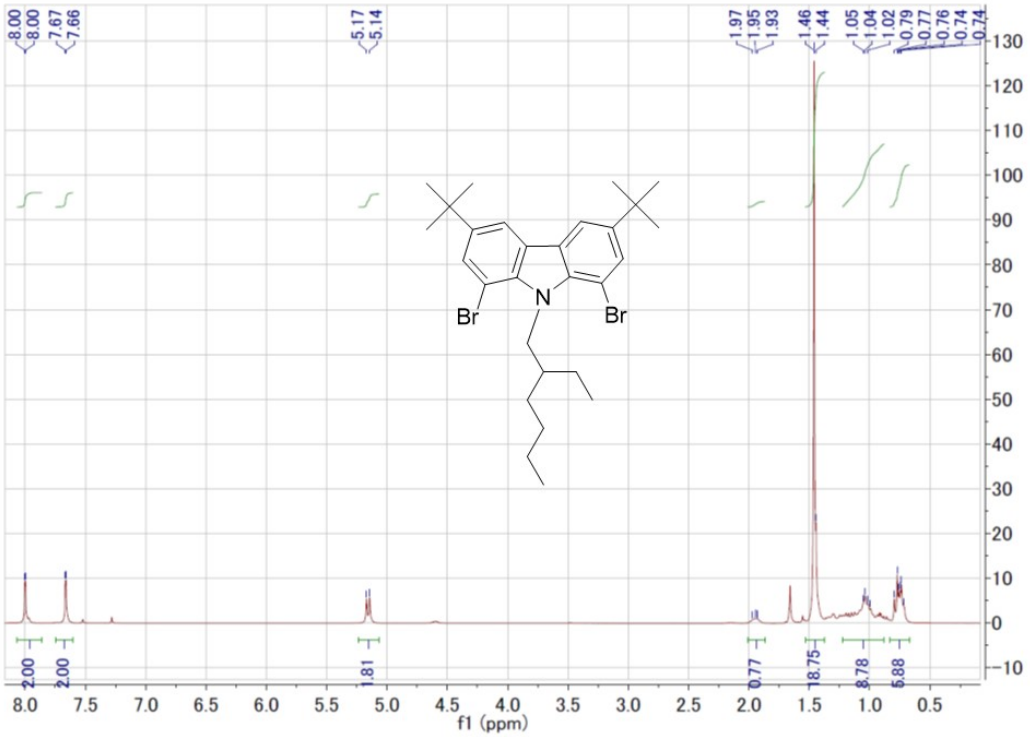


Fig. S3 ^{1}H-NMR spectrum of **3** in $CDCl_3$.

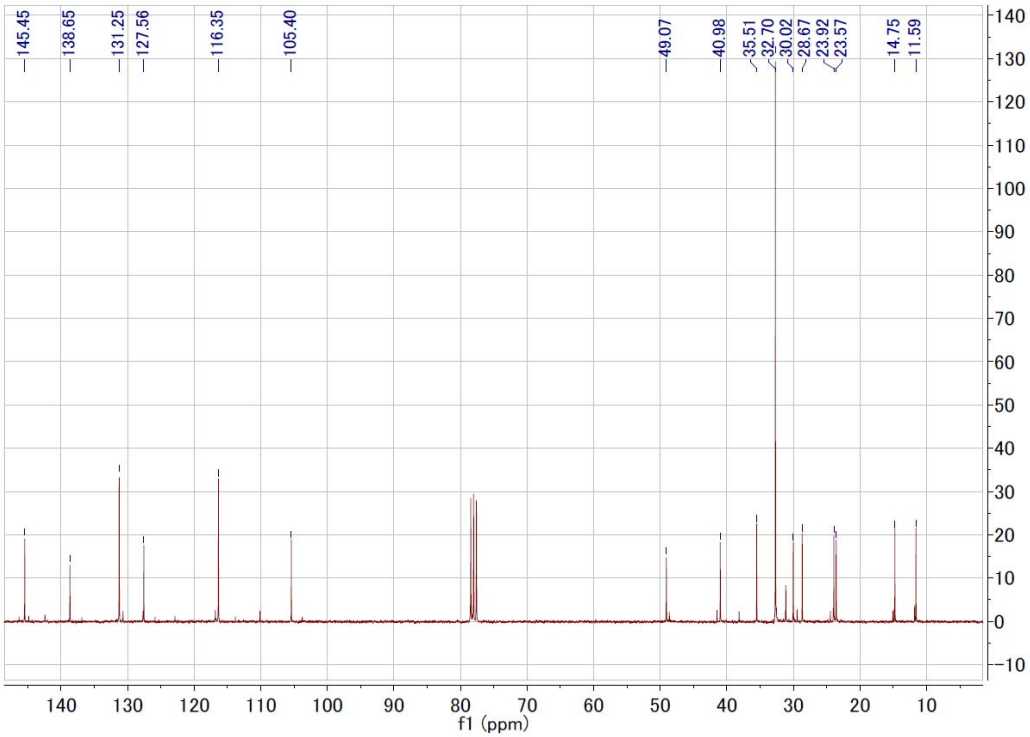


Fig. S4 ^{13}C-NMR spectrum of **3** in $CDCl_3$.

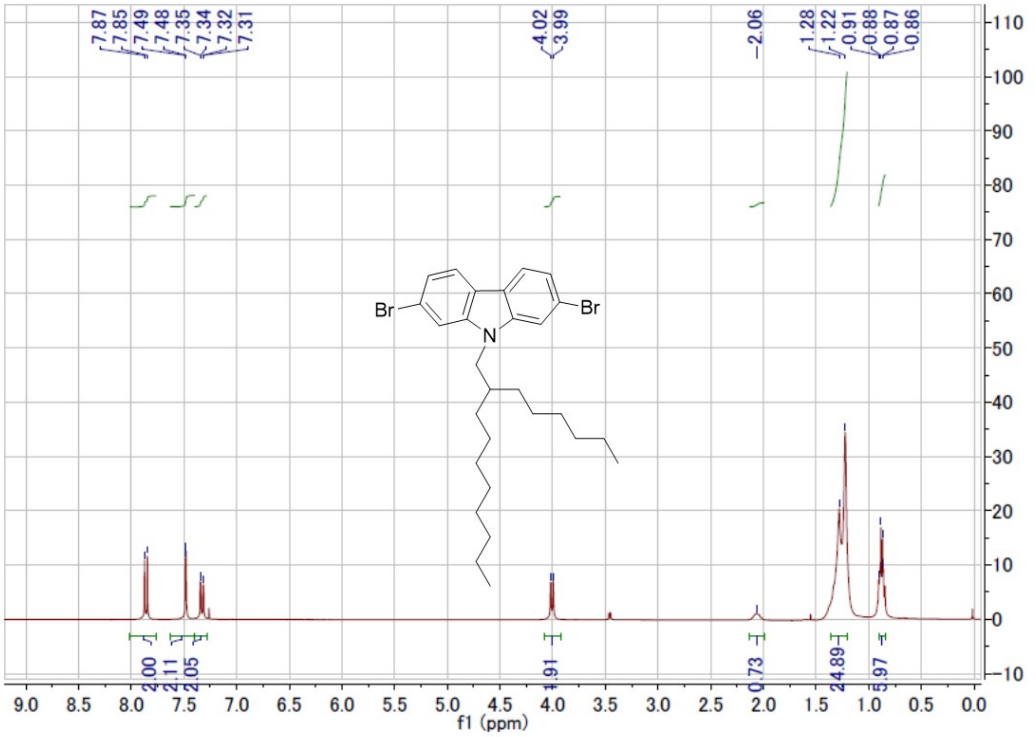


Fig. S5 ^{1}H-NMR spectrum of **4** in $CDCl_3$.

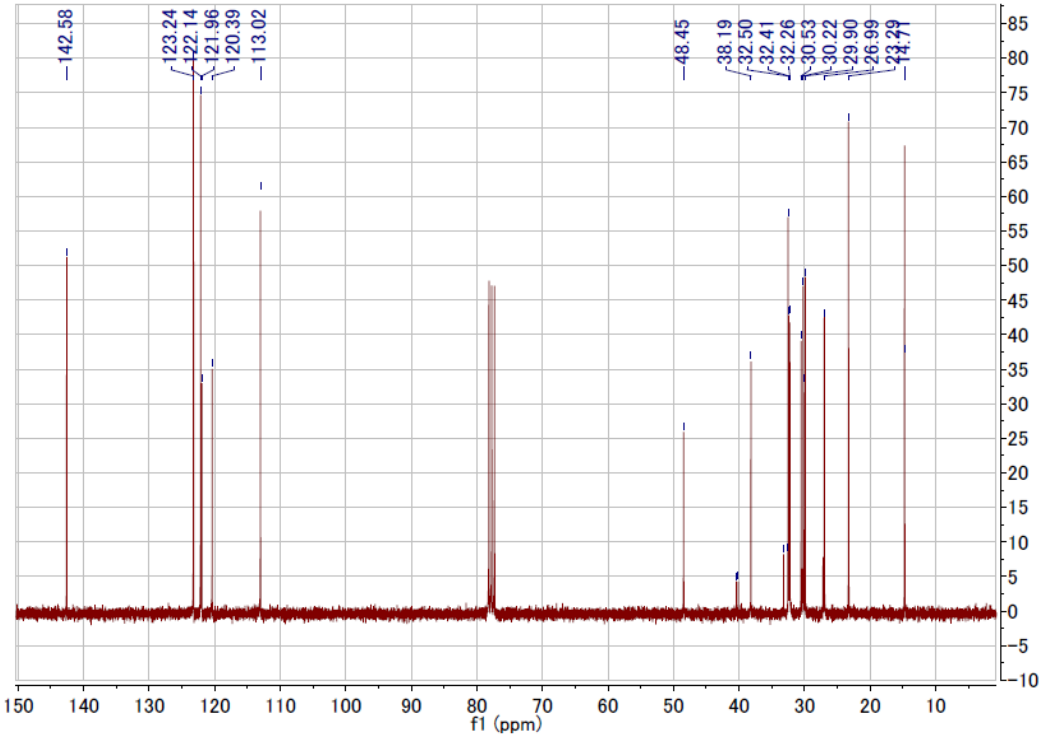


Fig. S6 ^{13}C-NMR spectrum of **4** in $CDCl_3$.

2. Direct arylation polycondensation

Table S1 Direct arylation polycondensation of **1** and EDOT

Run	Catalyst Ligand	Base	Acid	Solvent	Temp. Time	Yield M_n[a] M_w/M_n[a]
1[S4]	$Pd(OAc)_2$ 5mol% $PCy_3•HBF_4$ 5mol%	K_2CO_3 1.5 equiv	PivOH 30%	DMAc 3 mL	100 °C 6 h	73.9% 3.4 kg/mol 1.56
2[S5]	$Pd_2(dba)_3$ 5mol% P(*o*-OMePh)$_3$ 5mol %	K_2CO_3 1.5 equiv	PivOH 30%	DMAc 3 mL	100 °C 6 h	10.5% 0.7 kg/mol 1.52
3[S4,S6]	$Pd(OAc)_2$ 1mol% -	K_2CO_3 1.5 equiv	1-AdCOOH 30%	DMAc 2.5 mL	80 °C 30 min	7.4% 1.5 kg/mol 1.31
4[S4]	$Pd(OAc)_2$ 1mol% $PCy_3•HBF_4$ 1mol%	PivOK 1.5 equiv	-	DMAc 2.5mL	100 °C 30 min	73.5% 3.2 kg/mol 1.46

[a] Determined by GPC (THF eluent, calibrated by polystyrene standards)

3. Thermal analyses

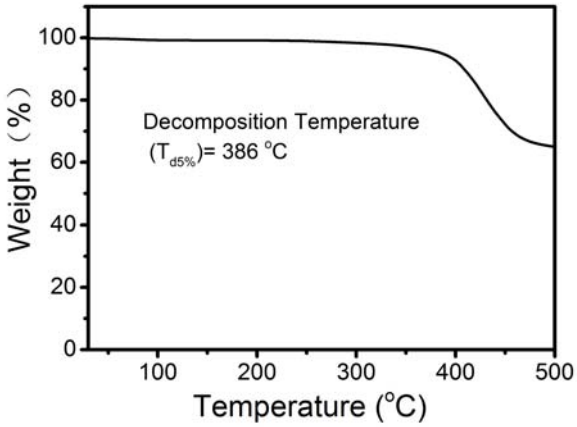


Fig. S7 Thermogravimetric analysis (TGA) curve of 3,6-Cbz-EDOT under nitrogen flow (50 mL min^{-1}) at the heating rate of 10 °C min^{-1}.

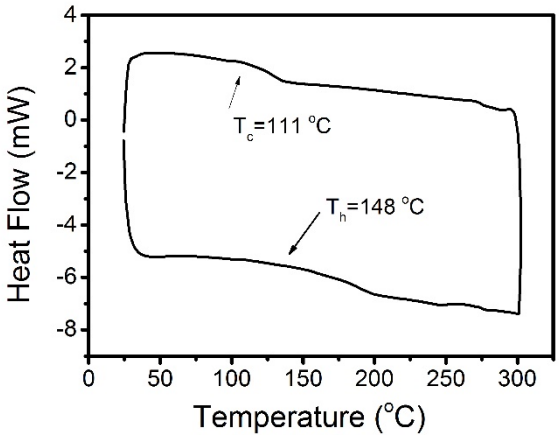


Fig. S8 Differential scanning calorimetry (DSC) curve of 3,6-Cbz-EDOT under nitrogen flow (50 mL min^{-1}) at the scanning rate of 10 °C min^{-1} (second heating and cooling processes).

4. Optical property

Fig. S9 Fluorescence images of 3,6-Cbz-EDOT (a) in CH_2Cl_2 and (b) in the thin film.

5. Electrochromism

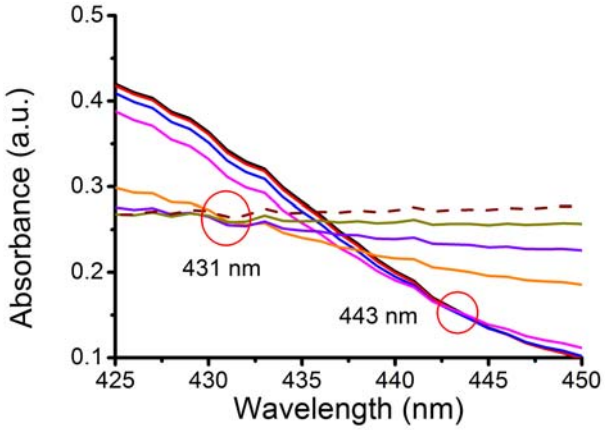


Fig. S10 Spectroelectrochemistry measurements of the 3,6-Cbz-EDOT film on an ITO electrode upon application from 0.0 V to 0.8 V with two isosbestic points.

6. References

S1 S.-H. Jung, H. K. Kim, S.-H. Kim, Y. H. Kim, S. C. Jeoung and D. Kim, *Macromolecules*, 2000, **33**, 9277.
S2 F. Dierschke, A. C. Grimsdale and K. Müllen, *Synthesis*, 2003, 2470.
S3 T. Michinobu, H. Osako and K. Shigehara, *Macromol. Rapid Commun.*, 2008, **29**, 111.
S4 J. Kuwabara, K. Yamazaki, T. Yamagata, W. Tsuchida and T. Kanbara, *Polym. Chem.*, 2015, **6**, 891.
S5 M. Wakioka, N. Ichihara, Y. Kitano and F. Ozawa, *Macromolecules*, 2014, **47**, 626.
S6 Y. Fujinami, J. Kuwabara, W. Ku, H. Hayashi and T. Kanbara, *ACS Macro Lett.*, 2012, **1**, 67.