Donor-Acceptor Conjugated Ladder Polymer via Aromatization-Driven Thermodynamic Annulation

Jongbok Lee,[1] Alexander J. Kalin,[1] Chenxu Wang,[2] Julia T. Early,[1] Mohammed Al-Hashimi,[3] and Lei Fang[1,2]*

---

1. Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX, USA

2. Department of Materials Science & Engineering, Texas A&M University, 3003 TAMU, College Station, TX, USA

3. Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar

---

Supporting Information

***Correspondence Address**

Professor Lei Fang

Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77843-3255, USA

Tel: +1 (979) 845 3186

E-Mail: fang@chem.tamu.edu

Table of Contents

1. General information 3

2. Synthesis 5

3. Size Exclusion Chromatography (SEC)...9

4. Lippert-Mataga Solvatochromism Plot 10

5. Charge Transfer Complex 12

6. Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)......14

7. Cyclic Voltammetry (CV) 14

8. ^{1}H and ^{13}C NMR Spectra 15

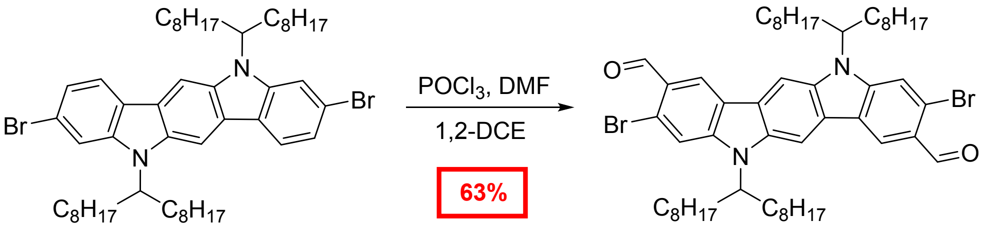
9. Reference 20

1. General information

Starting materials and reagents were purchased from Aldrich, Alfa Aesar, TCI, and Acros, and were used as received without further purification unless specified. Toluene and DMF were dried using Inert Technology pure solvent system (PureSolv-MD-5a) and used without further treatment. Anhydrous THF was distilled with Na/benzophenone before uses. Anhydrous 1,2-dichloroethane and 1,4-Dioxane were purchased from Acros. 4,7-dibromo-5,6-bis(bromomethyl)-2,1,3-benzothiadiazole[1] and 3,9-dibromo-5,11-dihydro-5,11-di(1-octylnonyl)indolo[3,2-*b*]carbazole (**S1**)[2] were synthesized according to reported procedures in literatures. Analytical thin-layer chromatography (TLC) tests were performed on glass that was precoated with silica gel 60-F_{254} (Sorbtech). Flash column chromatography was carried out using a Biotage® Isolera™ Prime with various sizes of SiO_2 Biotage ZIP® cartridges. UV-visible absorption spectra and fluorescence emission spectra were recorded using a Shimadzu UV-2600 and a Horiba Fluoromax-4 spectrometer, respectively. UV-visible-Near IR spectra were measured on a Hitachi U-4100 spectrometer. ^1H and ^{13}C NMR spectra were obtained on a 500 MHz Varian Inova at room temperature unless specified. The NMR data were processed in MestReNova 6.1.0. Chemical shifts were reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ($CDCl_3$: δ 7.26 for ^1H and 77.16 for ^{13}C at room temperature. Size exclusion chromatography (SEC) was performed on Tosoh EcoSEC (HLC-8320GPC) in THF solution at 40 °C with a flow rate of 0.4 mL/min through TSKgel SuperHM-M and TSKgel SuperH-RC columns. The molecular weights were calculated based on the retention time, using a calibration curve constructed from polystyrene standards. Preparative SEC was performed in chloroform solution at room temperature using a JAI recycling preparative HPLC (LC-92XXII NEXT SERIES). High-resolution Thermal gravimetric analysis

(TGA) was recorded under nitrogen atmosphere with heating rate of 10 °C min^{-1} from 25 to 900 °C using TA Q500. High-resolution Matrix-assisted laser desorption/ionization (HR-MALDI) mass spectra and low-resolution atmospheric pressure chemical ionization (LR-APCI) mass spectra were measured on Applied Biosystems 4800 MALDI-TOF and a Thermo Scientific LCQ-DECA, respectively. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out in Sector 8-ID-E at the Advanced Photon Source, Argonne National Laboratory.[3] Beamline 8-ID-E operates at an energy of 10.91 keV and the images were collected from a Pilatus 1MF camera (Dectris), with two exposures for different vertical positions of the detector. Using the GIXSGUI package[4] for MATLAB (Mathworks), data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle. The beam size is 0.8 mm × 0.5 mm and the resolution ($\Delta E/E$) is 1×10^{-4}. Sample detector distance is 278 mm. Solid-state samples for GIWAXS were deposited on silicon wafers by spin-casting with the solutions (5 mg/mL in $CHCl_3$) at a spin rate of 1500 rpm and annealed at 250 °C or 500 °C for 30 min.

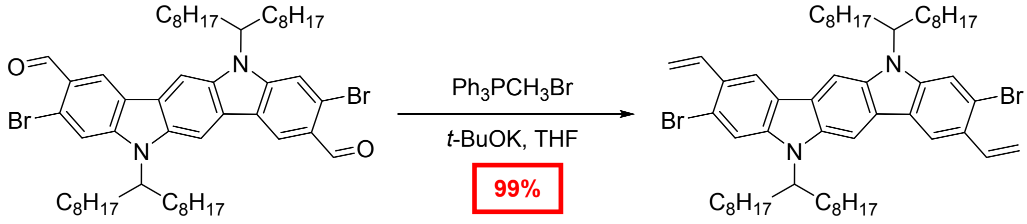
2. Synthesis



S1 **S2**

Scheme S1. Synthesis of compound **S2** from **S1** *via* Vilsmeier-Haak reaction.

S2 (3,9-dibromo-5,11-dihydro-5,11-di(1-octylnonyl)indolo[3,2-*b*]carbazole-2,8-dicarbaldehyde): In a 150 mL sealed tube, DMF (8.7 mL, 112.5 mmol) was added in anhydrous 1,2-DCE (30 mL) and cooled down to 0 °C under N_2. To the mixture was added phosphorus oxychloride (10.5 mL, 112.5 mmol) dropwise at 0 °C. After the reaction mixture was warmed to room temperature, compound **S1** (4.0 g, 4.5 mmol) was added into the flask, and the mixture was stirred at 95 °C for 48 h. The reaction was cooled down to room temperature and quenched with water. The aqueous mixture was basified to pH = 7 by 2M KOH solution. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layer was dried over $MgSO_4$, filtered through Celite, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:CH_2Cl_2 = 100:0 to 50:50) to give the product **S2** (2.7 g, 62%) as a yellow solid. ^1H NMR (500MHz, $CDCl_3$): δ 10.46 (s, 2H), 8.83, 8.81 (two s†, 2H), 8.27, 8.24, 8.13, 8.10 (four s†, 2H), 7.86, 7.77 (two s†, 2H), 4.68, 4.55 (two quint†, 2H), 2.40, 2.26 (two m†, 4H), 2.05 (m, 4H), 1.13 (m, 46H), 0.78 (t, *J* = 7.0 Hz, 12H). †Peak separations were observed due to the atropisomers by hindered rotation of α-branched alkyl chain. ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.98, 147.06, 143.82, 139.06, 138.93, 135.15, 125.15, 124.68, 124.36, 124.32, 123.72, 123.30, 123.11, 122.97, 122.76, 122.41, 122.04, 121.69, 104.08, 13.68, 103.39, 103.00, 100.96, 100.59, 57.94, 57.59, 33.77, 33.44, 31.84, 29.44, 29.23, 27.36, 26.99, 26.66, 22.70, 14.48, 14.19, 13.84. ^{13}C NMR showed multiple separated peaks due to the atropisomers. HR-MALDI: calcd for $C_{54}H_{78}Br_2N_2O_2$ $[M+H]^+$ *m/z* = 947.4488; found *m/z* = 947.4431.



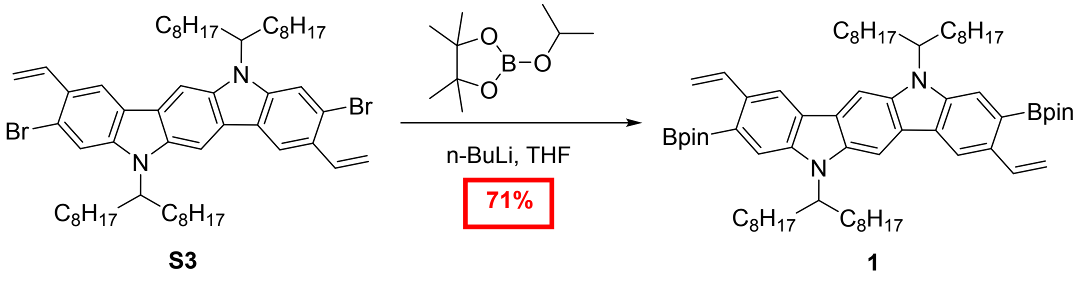
S2

S3

Scheme S2. Synthesis of compound **S3** from **S2** *via* Wittig reaction.

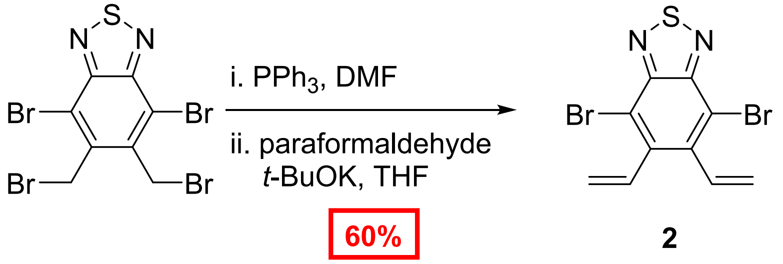
S3 (3,9-dibromo-2,8-diethenyl-5,11-dihydro-5,11-di(1-octylnonyl)indolo[3,2-*b*]carbazole): To the mixture of methyltriphenylphosphonium bromide (4.0 g, 11.2 mmol) in THF (80 mL) was added *t*-BuOK (1.18 g, 10.5 mmol) in small portions over 10 min at room temperature. Compound **S2** (2.5 g, 2.63 mmol) was added into the flask (covered with aluminum foil) with several crystals of 2,6-di-t-butyl-4-methylphenol (BHT). The mixture was stirred at reflux for 6 h. The reaction was quenched with water and diluted with CH_2Cl_2. The mixture was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layer was dried over $MgSO_4$, filtered through Celite, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane) to give the product **S3** (2.5 g, 99%) as a yellow solid. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.38, 8.35 (two s†, 2H), 8.14, 8.10, 8.00, 7.97 (four s†, 2H), 7.75, 7.59 (two s†, 1H), 7.26 (dd, J_1 = 17.5 Hz, J_2 = 11.0 Hz, 2H), 5.82 (dd, J_1 = 17.5 Hz, J_2 = 11.0 Hz, 2H), 5.34 (d, J = 11.0 Hz, 2H), 4.67, 4.48 (two br†, 2H), 2.42, 2.26 (two m†, 4H), 2.00 (m, 4H), 1.13 (m, 46H), 0.79 (t, J = 7.0 Hz, 12H). † Peak separations were observed due to the atropisomers by hindered rotation of α-branched alkyl chain. ^{13}C NMR (125 MHz, $CDCl_3$): δ

143.69, 142.79, 140.14, 138.25, 137.34, 137.12, 136.60, 136.36, 134.40, 127.47, 123.83, 123.55, 122.41, 122.17, 121.51, 120.92, 117.96, 117.78, 117.60, 114.77, 114.55, 113.85, 113.22, 112.49, 112.31, 105.12, 102.25, 101.95, 99.47, 99.26, 57.38, 57.02, 56.43, 33.88, 33.64, 31.88, 29.58, 29.46, 29.31, 27.04, 22.72, 14.21, 14.16. ^{13}C NMR showed multiple separated peaks due to the atropisomers. HR-MALDI: calcd for $C_{56}H_{82}Br_2N_2$ $[M+H]^+$ m/z = 944.4923; found m/z = 944.4905.



Scheme S3. Synthesis of compound **1** from **S3** *via* borylation.

1 (2,8-diethenyl-3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,11-dihydro-5,11-di(1-octylnonyl)indolo[3,2-*b*]carbazole): To the mixture of compound **S3** (1.07 g, 1.1 mmol) in anhydrous THF (20 mL) at –78 °C was added *n*-BuLi (1.4 mL, 2.31 mmol, 1.6 M in hexane) dropwise over 1 h and stirred for another 1 h at –78 °C. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.53 mL, 2.64 mmol) was added into the mixture, and the mixture was allowed to room temperature and stirred for 24 h. The reaction was quenched with water and diluted with CH_2Cl_2. The mixture was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layer was dried over $MgSO_4$, filtered through Celite, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:CH_2Cl_2 = 100:0 to 50:50) to give the product **1** (0.81g, 71%) as a yellow solid. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.46 (m, 2H), 8.20 (m, 2H), 8.17, 8.05 (two s†, 1H), 8.01 (s, 1H), 7.85 (s, 1H), 7.76 (dd, J_1 = 17.0 Hz, J_2 = 11.0 Hz, 2H), 5.85 (d, J= 17.0 Hz, 2H), 5.25 (d, J = 11.0 Hz, 2H), 4.71 (bs, 2H), 2.44, 2.37 (two m†, 4H), 2.02 (m, 4H), 1.43 (s, 24H), 1.14 (m, 46H), 0.80 (t, J = 7.0 Hz, 12H). †Peak separations were observed due to the atropisomers by hindered rotation of α-branched alkyl chain. ^{13}C NMR (125 MHz, $CDCl_3$): 151.67, 142.52, 138.76, 134.70, 133.83, 126.38, 125.67, 125.02, 124.16, 118.46, 116.21, 116.06, 115.88, 111.45, 102.36, 101.98, 99.55, 99.19, 83.73, 56.88, 56.39, 34.09, 33.77, 31.91, 29.69, 29.51, 29.38, 27.12, 26.98, 25.10, 22.73, 14.18. ^{13}C NMR showed multiple separated peaks due to the atropisomers. HR-MALDI: calcd for $C_{68}H_{106}B_2N_2O_4$ $[M+H]^+$ m/z = 1037.8417; found m/z = 1037.8499.



2

Scheme S4. Synthesis of compound **2** (4,7-dibromo-5,6-diethenyl-2,1,3-benzothiadiazole) from 4,7-dibromo-5,6-bis(bromomethyl)-2,1,3-benzothiadiazole.

2 (4,7-dibromo-5,6-diethenyl-2,1,3-benzothiadiazole): The mixture of compound 4,7-dibromo-5,6-bis(bromomethyl)-2,1,3-benzothiadiazole (3.0 g, 6.3 mmol) and PPh_3 (4.1 g, 15.8 mmol) in DMF (40 mL) was stirred at 80 °C for 18 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue and paraformaldehyde (4.3 g) were suspended in THF (70 mL) under N_2. While stirring, *t*-BuOK (2.1 g, 18.9 mmol) was added in small portions over 10 min. After 30 min, the reaction was quenched with water and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was dried over $MgSO_4$, filtered through Celite, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane) to give the product **S1** (1.7 g, 80%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.70 (dd, J_1 = 17.5 Hz, J_2 = 12.0 Hz, 2H), 5.76 (d, J_1 = 12.0 Hz, J2 = 1.5

Hz, 2H), 5.61 (dd, J_1 = 17.5 Hz, J_2 = 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.31, 140.56, 134.42, 124.49, 113.72. LR-APCI: calcd for $C_{10}H_6Br_2N_2S$ $[M+H]^+$ m/z = 346.87; found m/z = 346.93.

3. Size Exclusion Chromatography (SEC)

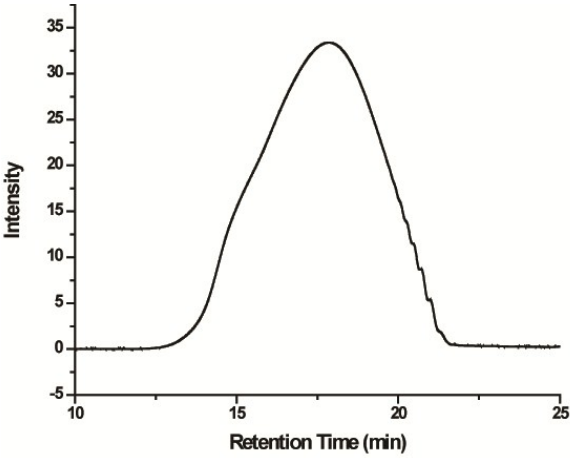


Fig. S1. Size exclusion chromatogram of **DACP** after purification by preparative recycling SEC. M_n^{SEC} = 43 kg/mol, PDI = 4.34. It is worthy to note that aggregation feature was observed as a shoulder peak in the high molecular weight region.

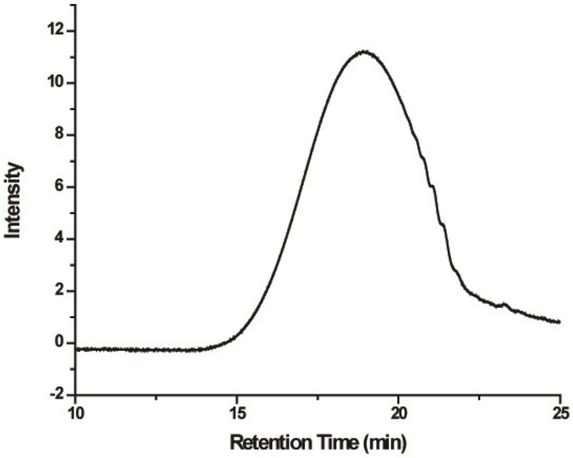


Fig. S2. Size exclusion chromatogram of **DALP** after Soxhlet extraction from $CHCl_3$. M_n^{SEC} = 21 kg/mol, PDI = 2.95.

4. Lippert-Mataga Solvatochromism Plot

The positive solvatochromism of **DALP** was demonstrated by a Lippert-Mataga plot using the Lippert-Mataga equation (1).[5]

$$\bar{\nu}_A - \bar{\nu}_E = \frac{2(\mu_G - \mu_E)^2}{hca^3}\Delta f + c \tag{1}$$

Herein, ν_A and ν_E are the absorption maximum and emission maximum in wavenumbers, μ_g and μ_E are, respectively, the ground and excited state dipole moments, h is Planck's constant, c is the speed of light in vacuum, a is the Onsager cavity radius, and Δf is the orientation polarizability. Stokes shift is generally described by the difference of absorption maximum and emission maximum. However, since **DALP** exhibits optically weak HOMO-LUMO transitions in the absorption spectrum, the Stokes shift of **DALP** represents the difference of the weak HOMO-LUMO absorption and the emission maximum. Unfortunately, it was difficult to obtain an accurate wavelength of the weak HOMO-LUMO absorptions in various solvents because the weak absorption shoulder (468 nm) observed in toluene became less characteristic in more polar solvents. Although the difference between absorption maxima and emission maxima does not depicts Stokes shift of **DALP**, the difference, which is more apparent, was plotted as a function of Δf, which is defined as the equation (2).[5]

$$\Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \left(\frac{n^2 - 1}{2n^2 + 1}\right) \tag{2}$$

where, ε is dielectric constant, and n is refractive index of a solvent.

Table S1. Summary of dielectric constants (ε),[6] refractive indices (n),[6] orientation polarizabilities (Δf), absorptions, emissions, and the difference between the absorptions and emissions in various solvents.

	ε	n	Δf	λ_{abs} (nm)	λ_{em} (nm)	$\Delta \nu$ (cm^{-1})
Toluene	2.38	1.4969	0.013	468	569	3792
Chlorobenzene	5.62	1.5248	0.143	469	591	4401
Chloroform	4.81	1.4459	0.148	467	590	4464
1,2-Dichlorobenzene	9.93	1.5514	0.186	470	608	4829
Tetrahydrofuran	7.58	1.4072	0.210	468	604	4811
Dichloromethane	8.93	1.4242	0.217	466	616	5225
1,2-Dichloroethane	10.37	1.4448	0.221	466	618	5278

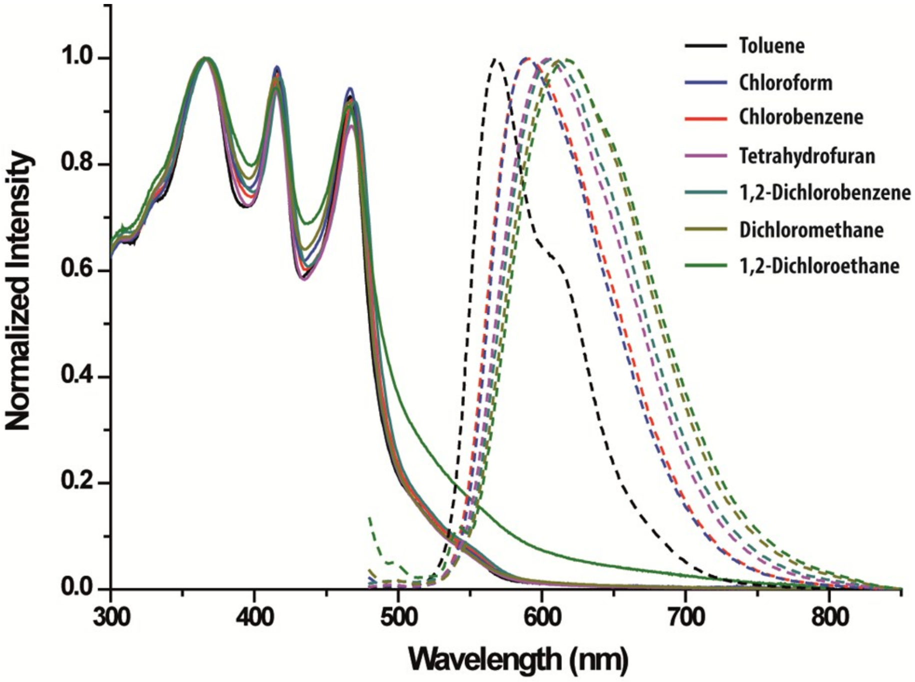


Fig. S3. UV-vis absorption and fluorescence emission spectra of **DALP** in different solvents.

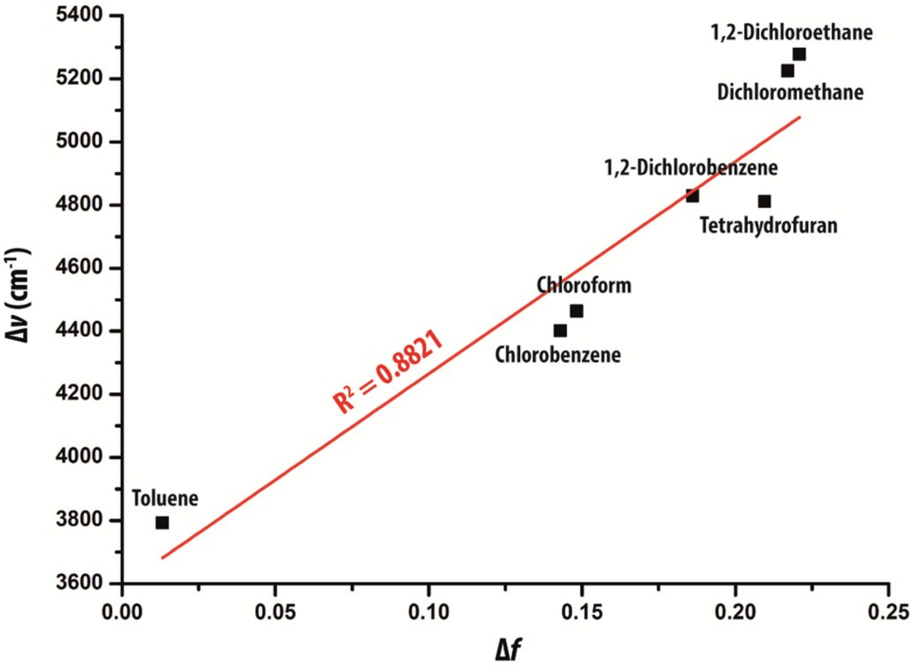


Fig. S4. Lippert-Mataga plot of **DALP**. The red line represents the linear fit ($R^2 = 0.8821$).

5. Charge Transfer Complex

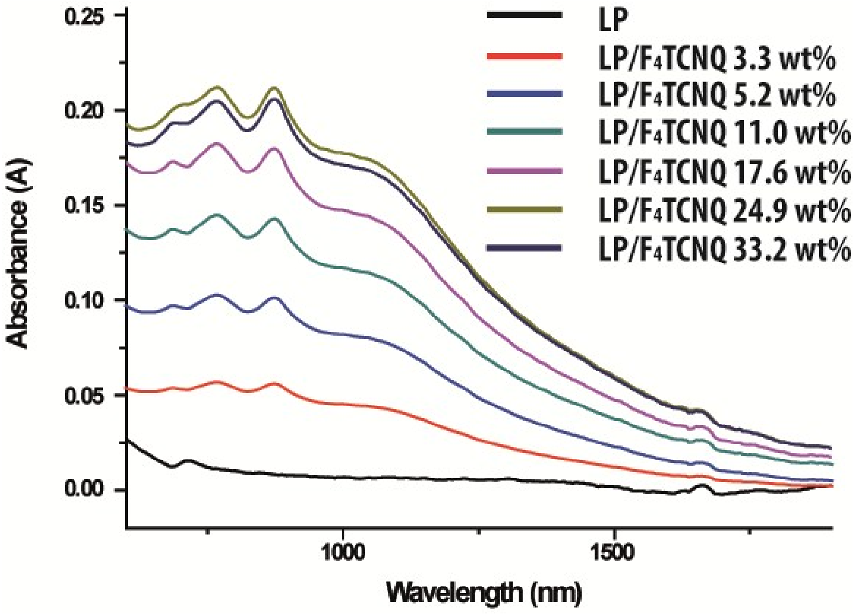


Fig. S5. UV-vis-NIR spectra of **LP** doped with various amounts of F$_4$TCNQ (from 0 wt% to 33.2 wt%).

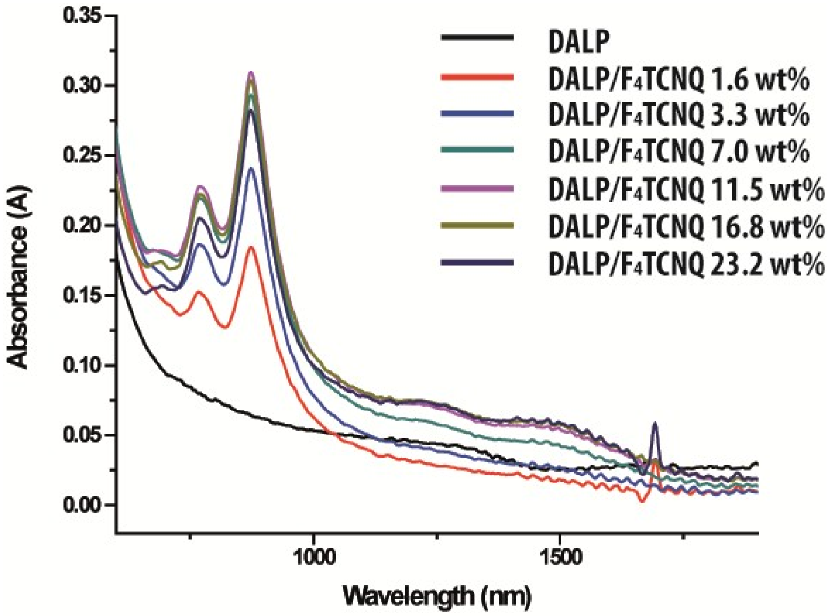


Fig. S6. UV-vis-NIR spectra of **DALP** doped with various amounts of F$_4$TCNQ (from 0 wt% to 23.2 wt%).

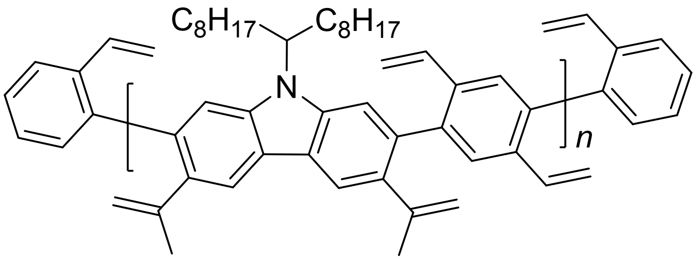


Fig. S7. Structural formula of **CP**, which is the polymeric precursor of **LP.**

6. Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)

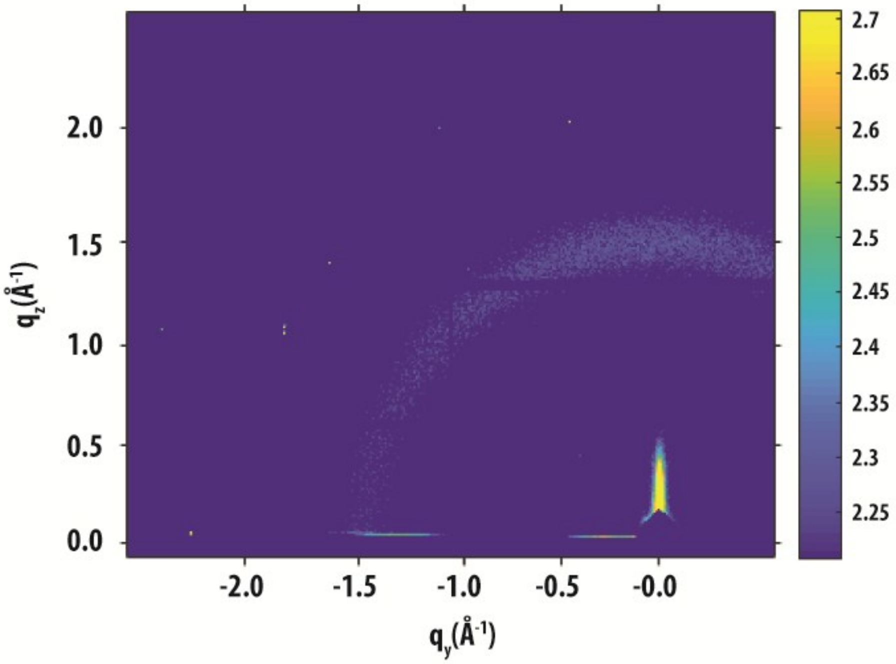


Fig. S8. GIWAXS image of as-cast film of **DALP**.

7. Cyclic Voltammetry (CV)

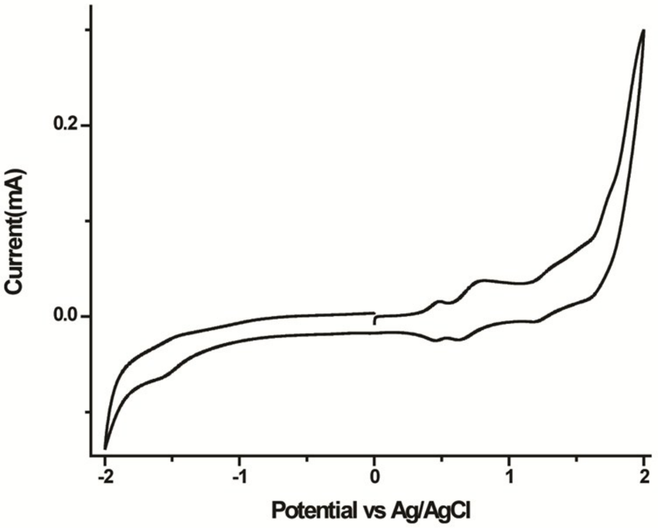


Fig. S9. Cyclic Voltammograms of DALP in DCM (0.1M [*n*-Bu_4N]PF_6) at scan rate of 20 mV/s.

8. ^{1}H and ^{13}C NMR Spectra

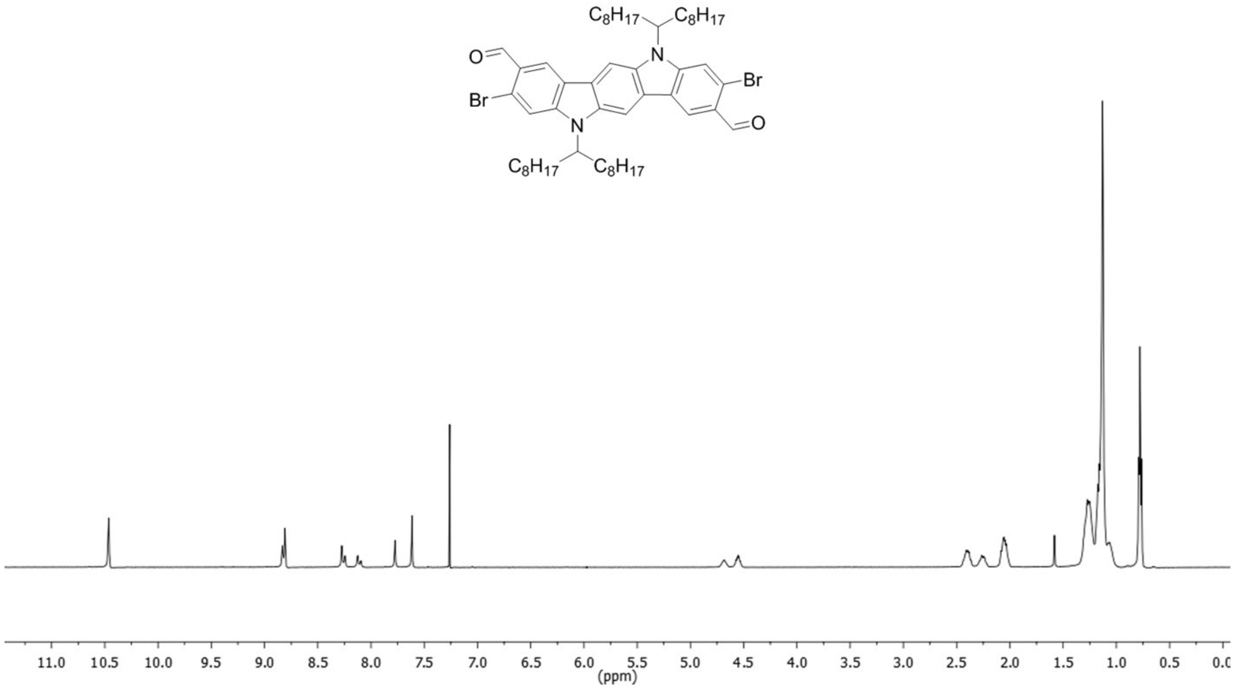


Fig. S10. ^{1}H NMR of **S2** (500 MHz, $CDCl_3$, RT).

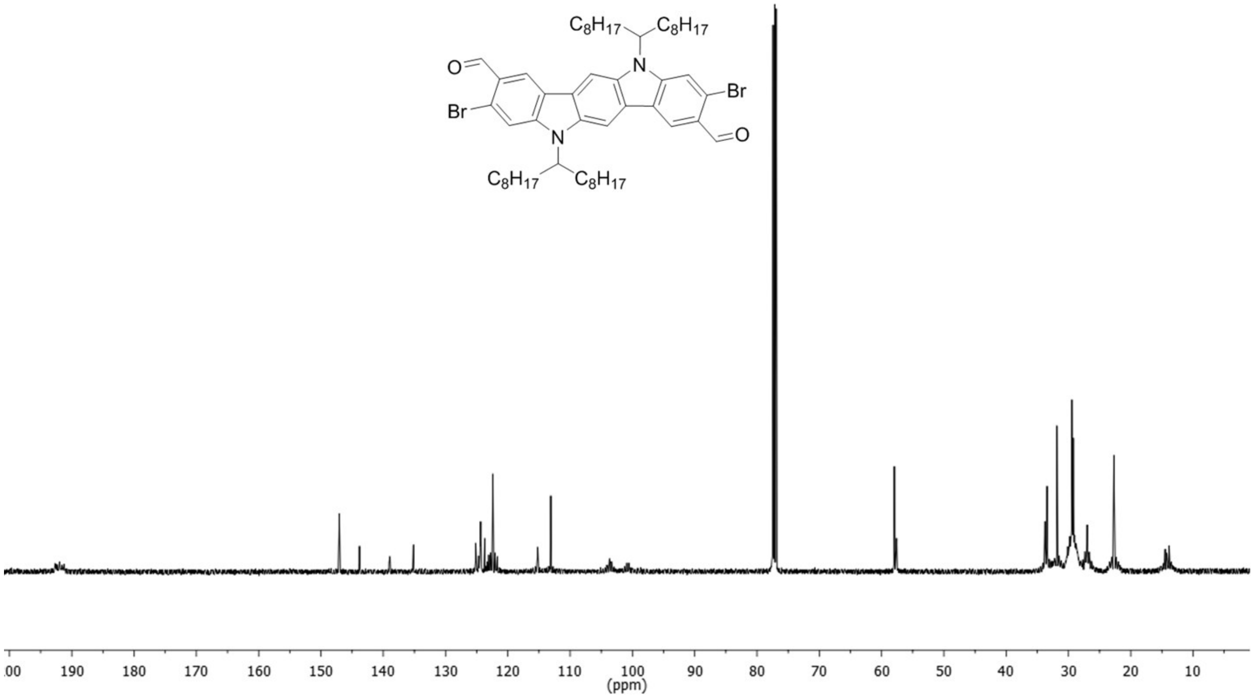


Fig. S11. ^{13}C NMR of **S2** (125 MHz, $CDCl_3$, RT).

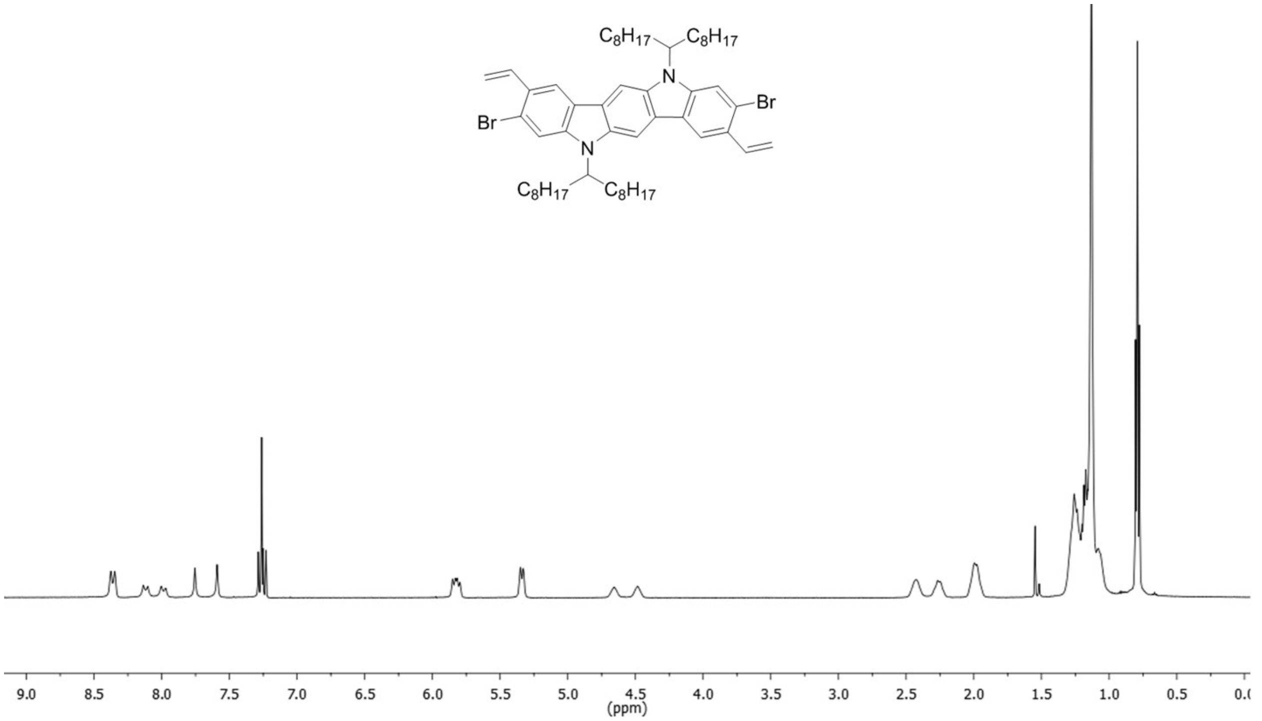


Fig. S12. ^{1}H NMR of **S3** (500 MHz, CDCl$_3$, RT).

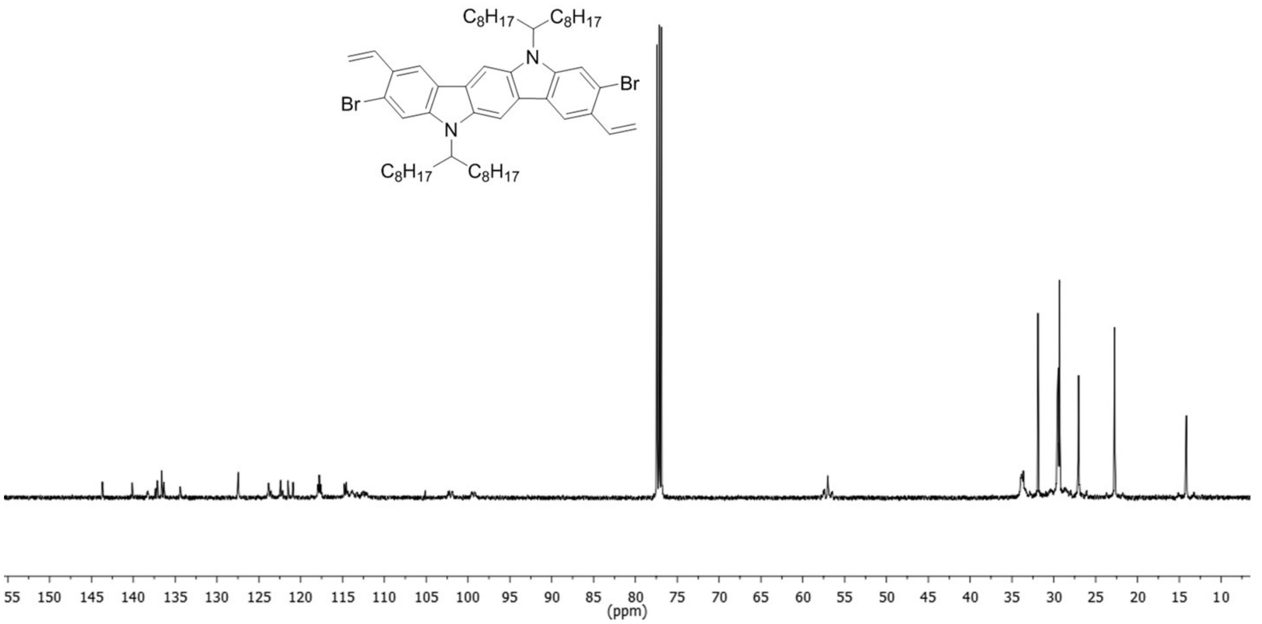


Fig. S13. ^{13}C NMR of **S3** (125 MHz, CDCl$_3$, RT).

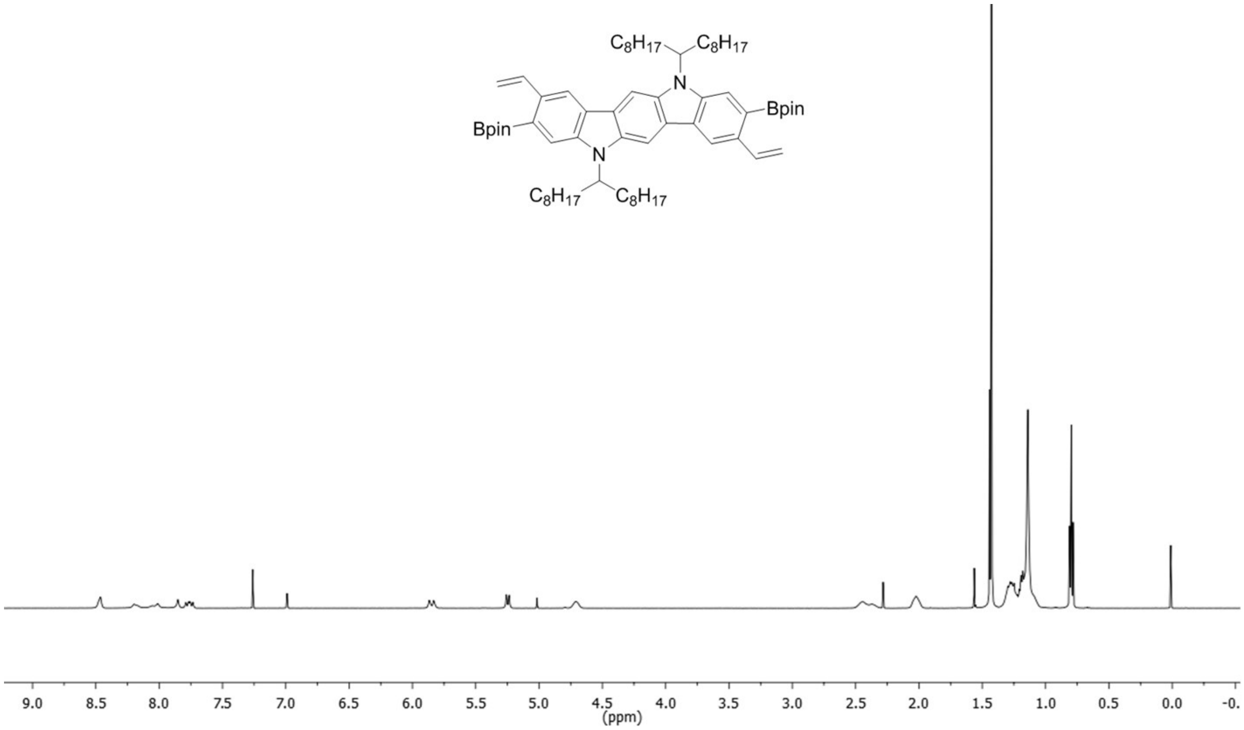


Fig. S14. ^{1}H NMR of **1** (500 MHz, CDCl$_3$, RT).

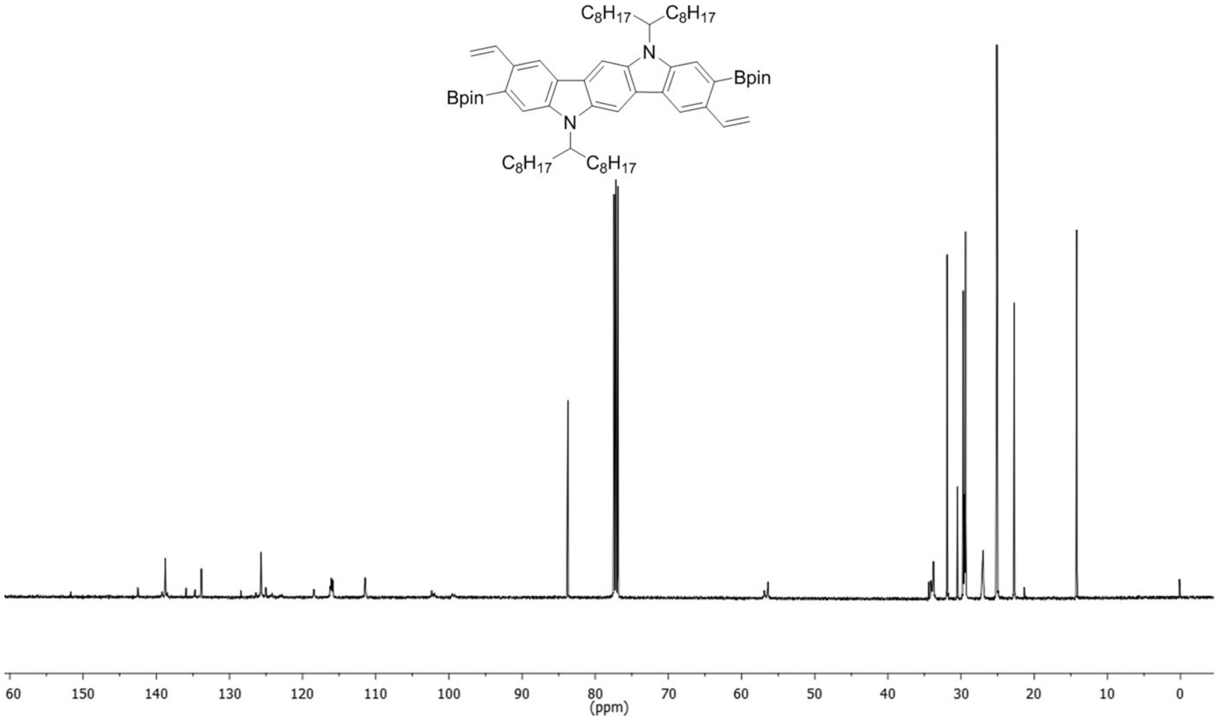


Fig. S15. ^{13}C NMR of **1** (125 MHz, CDCl$_3$, RT).

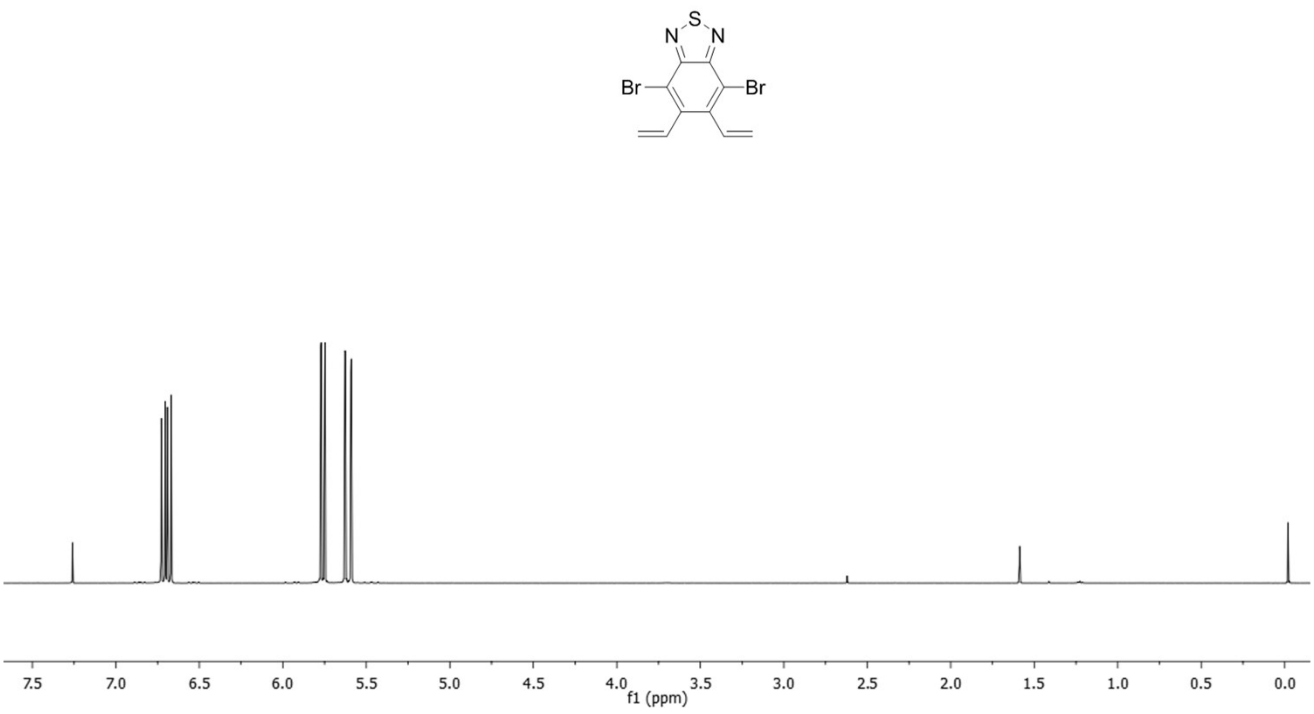


Fig. S16. ^{1}H NMR of **2** (500 MHz, $CDCl_3$, RT).

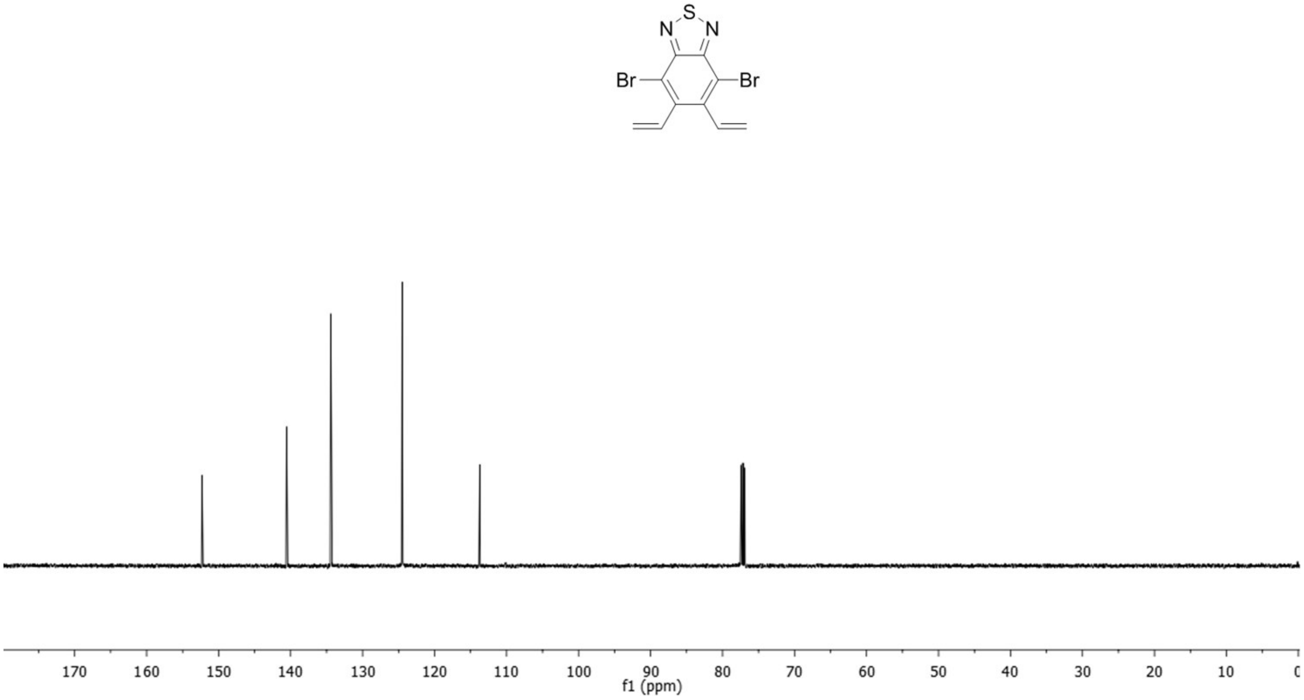


Fig. S17. ^{13}C NMR of **2** (125 MHz, $CDCl_3$, RT).

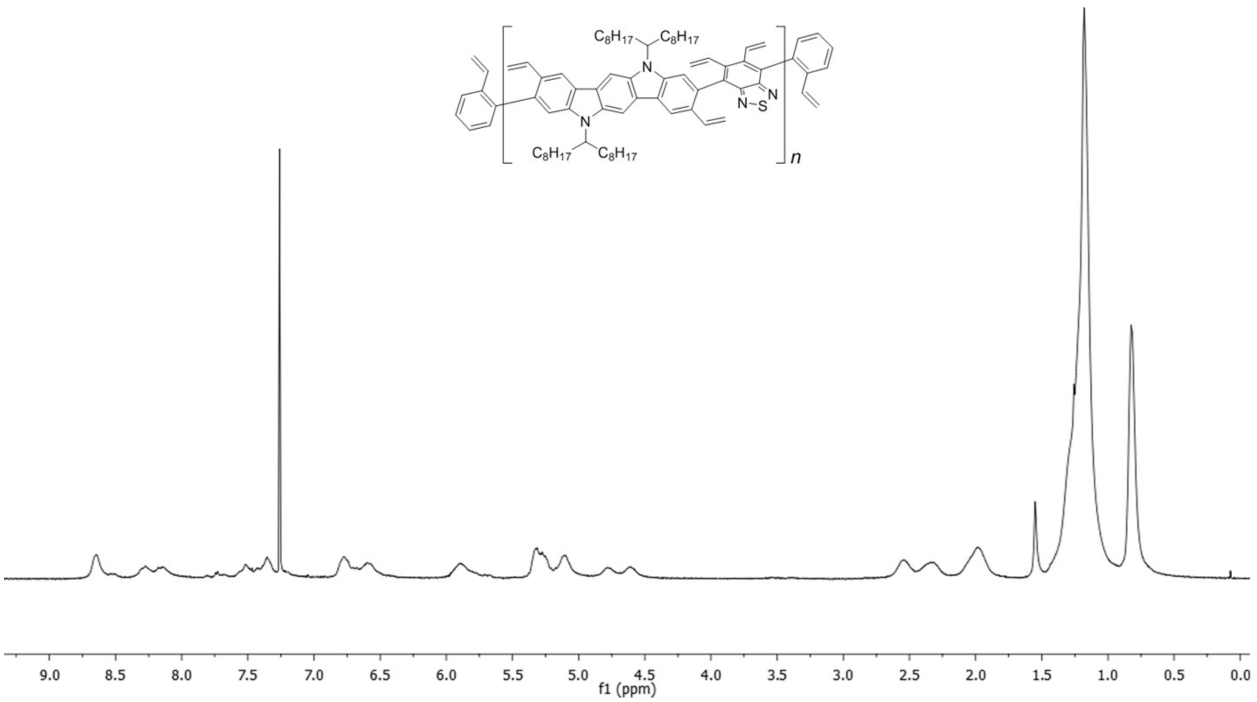


Fig. S18. ^{1}H NMR of **DACP** (500 MHz, $CDCl_3$, RT).

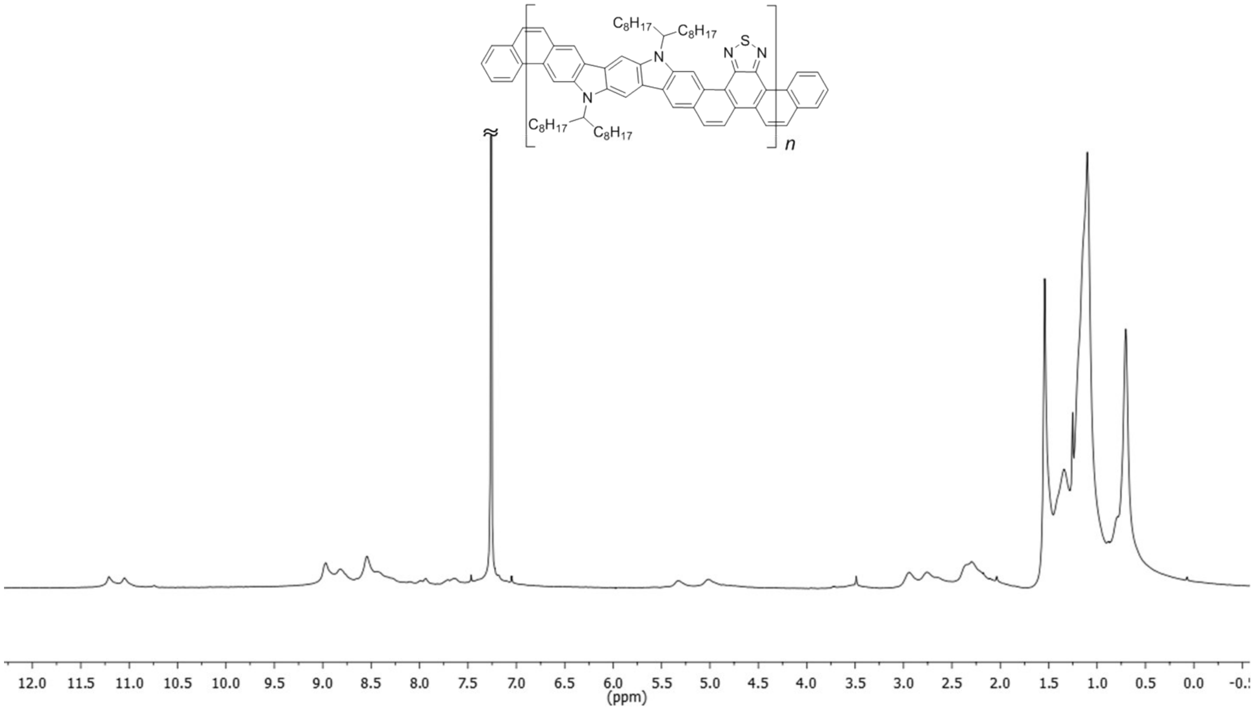


Fig S19. ^{1}H NMR of **DALP** (500 MHz, $CDCl_3$, RT).

9. Reference

1. K. -J. Yoon, J. S. Park, S. -J. Lee, M. Song, I. A. Shin, J. W. Lee, Y. -S. Gal, and S. -H. Jin, *J. Polym. Sci. A*, 2008, **46**, 6762-6769.

2. Y. Li, Y. Wu, S. Gardner, and B. S. Ong, *Adv. Mater.*, 2005, **17**, 849-853.

3. Z. Jiang, X. F. Li, J. Strzalka, M. Sprung, T. Sun, A. R. Sandy, S. Narayanan, D. R. Lee, and J. Wang, *J. Synchrot. Radiat.,* 2012, **19**, 627-636.

4. Z. Jiang, *GIXSGUI is available for download:*

http://www.aps.anl.gov/Sectors/Sector8/Operations/GIXSGUI.html.

5. a) N. Mataga and T. Kubota, *Ber. Bunsenges. Phys. Chem.* 1971, **75**, 603; (b) N. Mataga, Y. Kaifu, and M. Koizumi, M. *Bull. Chem. Soc. Jpn.* 1956, **29**, 465; (c) E. Z. Lippert, *Naturforschg.* 1955, **10a**, 541.

6. M. Montalti, A. Credi, L. Prodi, and M. T. Gandolfi, Handbook of Photochemistry, 3rd ed.;CRC Press:Boca Raton, **2006**