

Supporting Information to:
High Efficiency Dye-Sensitized Solar Cells with
Ferrocene-based Electrolytes

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Materials and Methods

Materials: All materials were purchased from commercial suppliers and used as received unless stated otherwise.

Working electrode preparation: The glass substrate used was 4mm thick $10 \Omega \square^{-1}$ conductive FTO (fluorine doped tin oxide) glass with high transparency in the visible range purchased from Nippon sheet glass. Mesoporous 4x4 mm TiO_2 films were printed using a commercial semi automatic screen printer and commercial 18 nm TiO_2 screen printing paste (PST-18NR, JGC Catalysts and Chemicals). The scattering paste was prepared from 400 nm particles mixed 5 to 1 by weight with 18 nm particles and an additional 3.5 parts ethyl cellulose and 30.5 parts terpineol. After a first sinter process (500°C) a TiCl_4 treatment was applied by immersing the films in a 20mM aqueous TiCl_4 solution and applying 70°C heat for 30min in a water saturated atmosphere. After another sintering process (500°C) the approximately 80°C warm films were immersed in a solution of 0.2 mM Carbz-PAHTDIT and 20.0mM chenodeoxycholic acid in a 3 : 2 mixture of chloroform and ethanol over 12 hours. N719 dye was purchased from dyesol and used as 0.5mM solution in 50% acetonitrile, 50% *tert*-butanol with a dyeing time of 12 hrs. The dyed films were washed in acetonitrile for 5 min to remove non-attached dye from the pores.

Counter electrode fabrication: Counter electrodes were prepared from 3mm thick $15 \Omega \square^{-1}$ conductive FTO (fluorine doped tin oxide) glass purchased from Nippon sheet glass. A 10mM chloroplatinic acid hexahydrate solution in ethanol was doctor bladed onto the substrate and pyrolysed for 15 min at 450°C .

Electrolyte Fabrication: All electrolytes used were prepared using anhydrous solvents, deoxygenated by freeze-drying and stored in a nitrogen glove box. Iodide, propyl-methyl imidazolium iodide (PMII), chenodeoxycholic acid (cheno) and guanidinium thiocyanate (GuSCN) were purchased from commercial suppliers in high purity and used as received. The *tert*-butylpyridine (*t*-BP) was distilled under nitrogen atmosphere and then stored in

the glovebox. After the addition of *t*-BP the cheno precipitated, but redissolved after 1 minute of stirring.

Table S1: Electrolyte compositions used throughout the complete study.

	Ratio ox : red	I ₂	PMII	<i>t</i> -BP	Cheno	GuSCN	Solvent
I-DSC	1:5	0.05M	0.6M	0.5M		0.1M	ACN:VN 85:15
I-DSC-C	1:5	0.05M	0.6M	0.5M	0.01M	0.1M	ACN:VN 85:15
		FcPF ₆	Fc	<i>t</i> -BP	Cheno		
Fc-DSC	1:2	0.05M	0.1M	0.5M			ACN
Fc-DSC-C	1:2	0.05M	0.1M	0.5M	0.01M		ACN

Cell assembly: The dried working electrode and the counter electrode were assembled using a 25 μ m thick Surlyn gasket (Solaronix) of the dimensions 5x6mm. A pneumatic finger was used to apply pressure while heating through the counter electrode. The cells were then transferred into a nitrogen glove box and vacuum backfilled through a predrilled hole in the counter electrode. The backfilling hole was sealed at 150°C using a square of aluminium backed Surlyn prepared by melting 25 μ m Surlyn onto aluminium foil at 100°C.

Device characterization

IV Characterization: A sun simulator (Oriel) fitted with a filtered 1,000W xenon lamp was used to provide simulated solar irradiation (AM1.5, 1,000W m⁻²). Current–voltage curves were recorded using a Keithley 2400 source meter. The output of the light source was adjusted using a calibrated silicon photodiode (Pecell Technologies). The photodiode was fitted with a color filter provided by the supplier, to minimize the optical mismatch between the calibration diode and the dye-sensitized solar cells. The light intensity was adjusted by using a filter wheel equipped with a series of mesh filters.

IPCE: The incident photon conversion efficiency (IPCE) was measured using a 150W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 260) as a monochromatic light source. The illumination spot size was chosen to be slightly smaller than the active area of the DSC test cells. IPCE photocurrents were recorded under short-circuit conditions using a Keithley 2400 source meter. The monochromatic photon flux was quantified by means of a calibrated silicon photodiode (Peccell Technologies).

UV-Vis: UV-Vis data was acquired using a Cary 5000 (Varian) spectrometer and a DRA 2500 integrating sphere. 2.2 μm transparent, 4.4 μm scattering double layer films were used for the absorption study.

IMVS-IMPS: For IMPS and IMVS measurements a blue LED was modulated to a depth of ca. 2% using a Stanford lock-in-amplifier (SR810) and purpose built LED driver with an adjustable DC offset. The illumination intensity was varied using a set of neutral density filters. All experiments were performed in an earthed Faraday dark-box to eliminate electrical noise at low light intensities. Photocurrents were measured using a battery powered current preamplifier (Stanford SR570) and photovoltages measured using a purpose built battery powered high impedance voltage follower (input impedance $10^{12} \Omega$). The phase and amplitude of the resultant AC photocurrent (or photovoltage) were captured using the lock-in amplifier (SR810) under computer control (Labview).

Charge Extraction: A charge extraction setup identical as in Duffy *et al* (*Electrochem. Commun.* **2**, 658 (2000)) was used to determine the charge stored in the films. Fig S1 shows the extracted charge per film area vs. open circuit voltage.

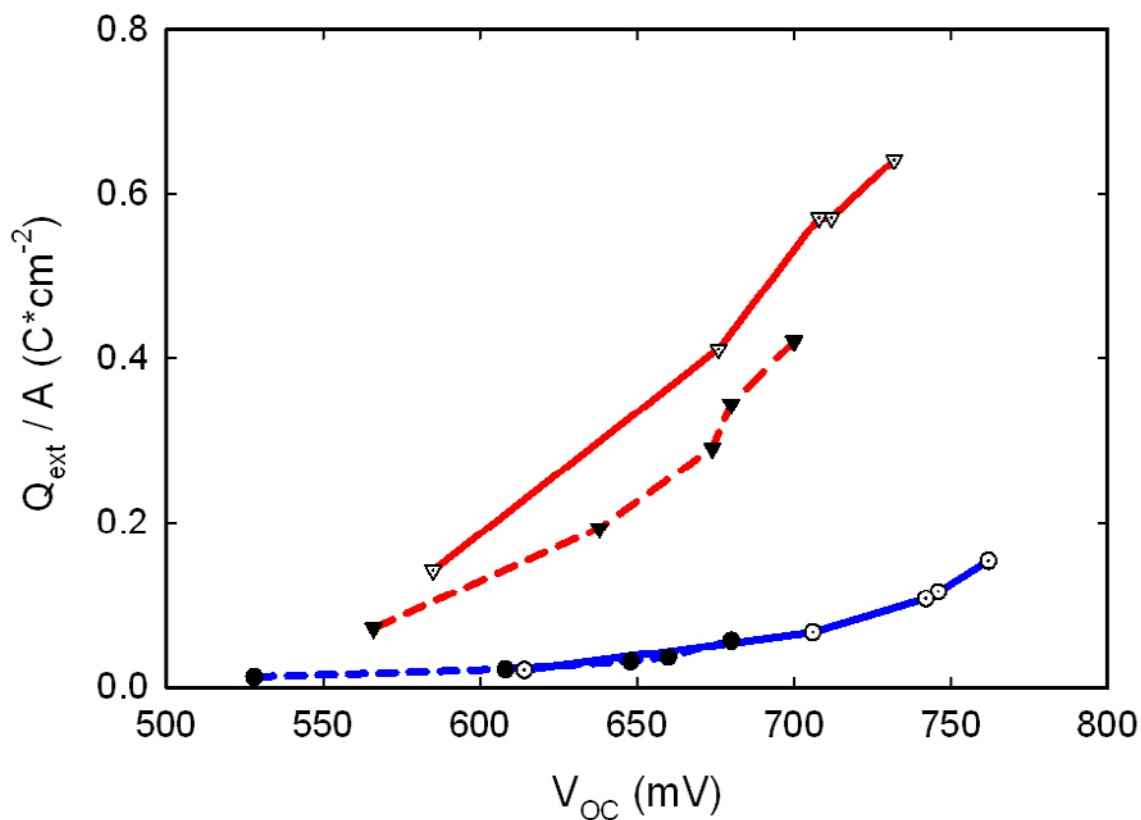


Figure S1: Extracted charge per film area vs open circuit voltage. Red I-DSC, blue Fc-DSC. Cells containing cheno in the electrolyte (solid) and cells without cheno (dashed).

Table S2: Tabulation of IV data measured in this study

#	Electrolyte composition ^a						Photovoltaic performance			
	Solvent	Film ^b	I ₂	PMII	<i>t</i> -BP	Cheno	J _{sc} ^c	V _{oc} ^d	FF	η ^e
N719	ACN / VN	2.2+4.4	0.05	0.6	0.5	0	10.83	830	0.75	6.8
N719	ACN / VN	12+6	0.05	0.6	0.5	0	14.4	780	0.72	8.2

#	Electrolyte composition ^a						Photovoltaic performance			
	Solvent	Film ^b	I ₂	PMII	<i>t</i> -BP	Cheno	J _{sc} ^c	V _{oc} ^d	FF	η ^e
I-DSC	ACN / VN	2.2+4.4	0.05	0.6	0.5	0	13.3	735	0.62	6.1
I-DSC	ACN / VN	12+6	0.05	0.6	0.5	0	12.1	741	0.7	6.3
I-DSC-C	ACN / VN	2.2+4.4	0.05	0.6	0.5	0.01	12.3	742	0.67	6.1

#	Electrolyte composition ^a						Photovoltaic performance			
	Solvent	Film ^b	Fc	FcPF ₆	<i>t</i> -BP	Cheno	J _{sc} ^c	V _{oc} ^d	FF	η ^e
Fc-DSC	ACN	2.2+4.4	0.1	0.05	0.5	0	9.6	8.15	0.75	5.9
Fc-DSC-C	ACN	2.2+4.4	0.1	0.05	0.5	0.01	12.2	8.42	0.73	7.5
N719-Fc-C	ACN	2.2+4.4	0.1	0.05	0.5	0.01	0.80	579	0.71	0.33

^aAll concentrations are listed in mol L⁻¹, ^b film thickness is measured in x μm (transparent) + y μm (scattering). ^cThe short circuit current J_{sc} is measured in mA cm⁻², ^dthe open circuit voltage in mV, and ^e efficiency η in %. Solvents are acetonitrile (ACN) and valeronitrile (VN)

Synthesis, Photophysical and Electrochemical Properties of 3-(5-{6-[5-(2-{4-[Bis-(4-carbazol-9-yl-phenyl)-amino]-phenyl}-vinyl)-3-hexyl-thien-2-yl]-dithieno[3,2-b;2',3'-d]thiophen-2-yl}-4-hexyl-thien-2-yl)-2-cyano-acrylic acid (Carbz-PAHTDTT, S9)

General Experimental

¹H NMR spectra were recorded on Varian Unity 500 (500 MHz) instruments, using deuteriochloroform (or other indicated solvents) as reference or internal deuterium lock.

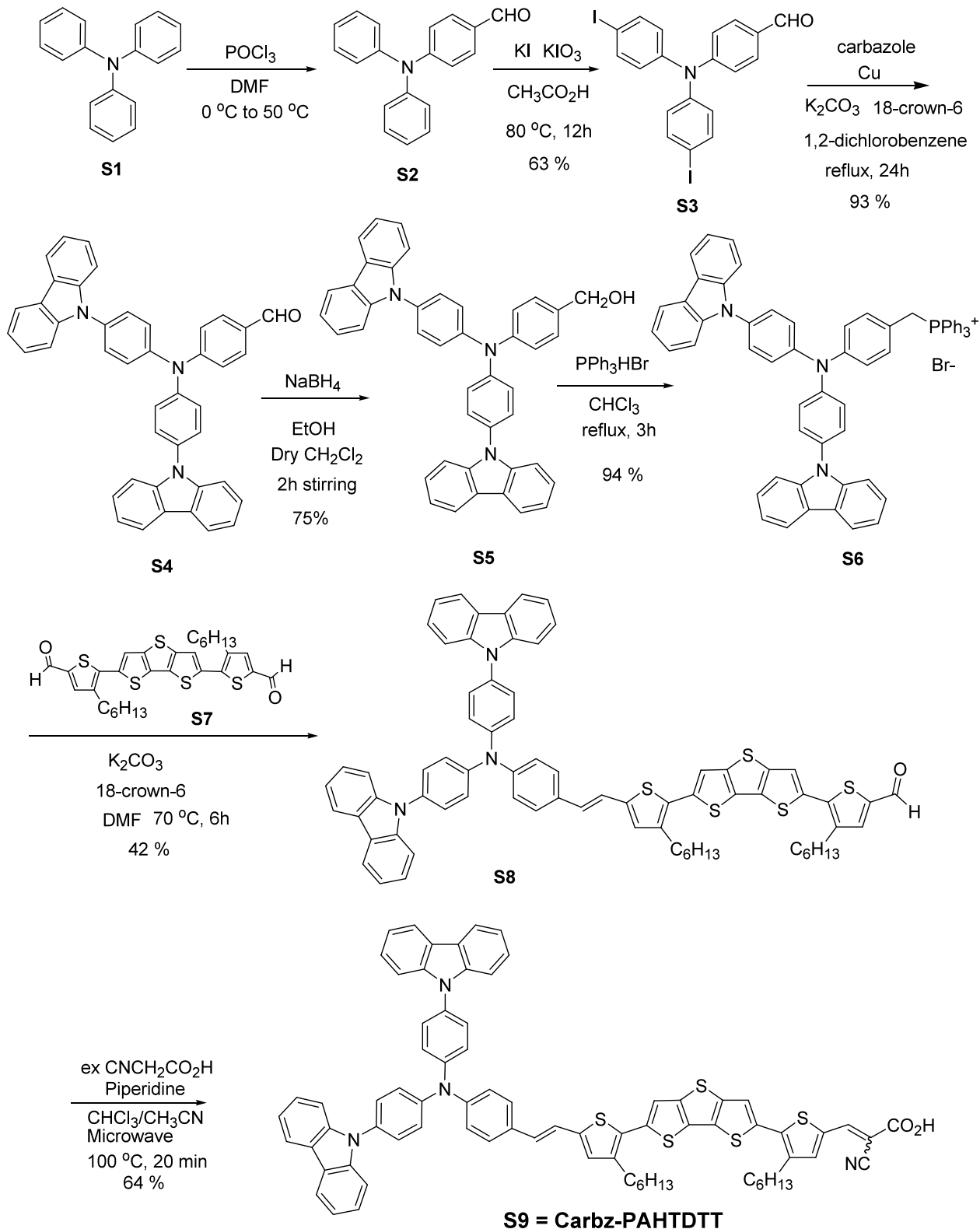
¹³C NMR spectra were recorded on Varian Unity 500 (125 MHz) instruments using the central resonance of the triplet of CDCl₃ at δ 77.0 ppm (or other indicated solvents) as an internal reference.

Flash chromatography was carried out, unless stated otherwise, on silica gel [Merck Kieselgel 60 (230 – 400 mesh)] under a pressure of nitrogen. Analytical thin layer chromatography (TLC) was done on pre-coated 0.2 mm thick Merck Kieselgel 60 F₂₅₄ silica gel plates and visualized by absorption of UV light.

Solvents were purchased from Aldrich. Where appropriate and if not stated otherwise, all reactions were performed in flame-dried apparatus under an atmosphere of dry nitrogen.

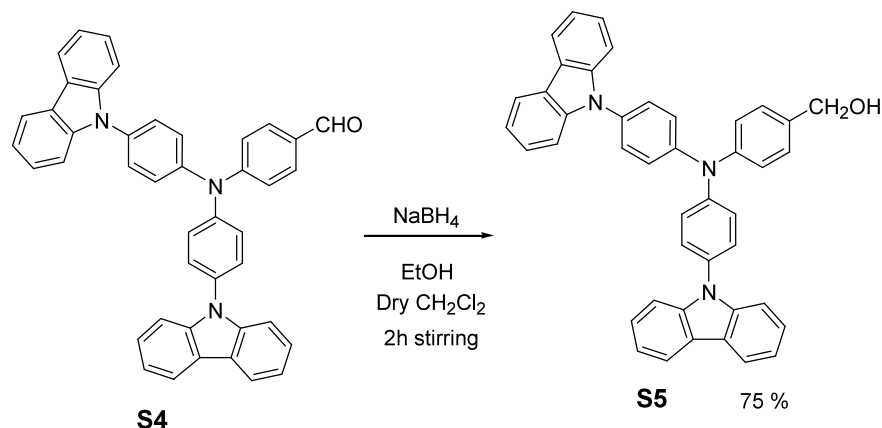
IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using a Cary 50 UV-vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Microwave reaction was performed using a Biotage (Initiator EXP EU). Melting points were determined on a Büchi 510 melting point apparatus.

Scheme 1: Synthesis of Carbz-PAHTDTT (S9)



The synthesis of the intermediates (**S2**), (**S3**) and (**S4**) were carried out as previously reported by Z. Ning et al [*Adv. Funct. Mater.* **17**, 3799 (2007)].

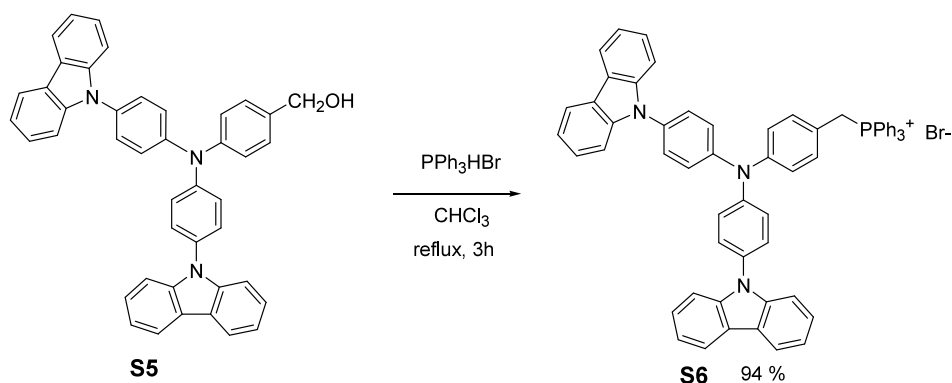
{4-[Bis-(4-carbazol-9-yl-phenyl)-amino]-phenyl}-methanol (**S5**)



To a solution of NaBH₄ (136 mg, 3.6 mmol) in dry dichloromethane (30 mL) and anhydrous ethanol (10 mL), the aldehyde **S4** [*Adv. Funct. Mater.* **17**, 3799 (2007)] (2.2 g, 3.6 mmol) was added rapidly, and the bath was stirred at room temperature for 2h. The solution was poured into water (50 mL) with vigorous stirring and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried with anhydrous sodium sulfate and then rotary evaporated to remove the solvent, to give the alcohol **S5** as a pale yellow solid (1.6 g, 2.7 mmol, 75%). m.p. 145 °C, R_f = 0.44 (2:1 pet. spirit 40-60 / EtOAc).

¹H NMR (500 MHz, CDCl₃): δ 4.73 (2 H, s), 7.30-7.35 (6 H, m), 7.40-7.47 (10 H, m), 7.49-7.51 (8H, m), 8.17 (2 H, d, J = 7.5 Hz), ¹³C NMR (125 MHz, CDCl₃): δ 64.97, 109.77, 119.83, 120.30, 123.26, 124.70, 125.23, 125.87, 128.04, 128.61, 132.21, 136.46, 140.97, 146.59, 146.76 m/z (EI) (rel. intensity) 606.3[100, (M+H)⁺], 607.3[50, (M+2H)⁺], 608.3[12, (M+3H)⁺]. m/z (EI): 606.2499 [M+H]⁺ calcd. for C₄₃H₃₂N₃O 605.2545. FT-IR (neat cm⁻¹): 3369, 3043, 1624, 1599, 1507, 1479, 1452, 1312, 1284, 1230, 1182, 1148, 1119, 1014, 832, 748, 724.

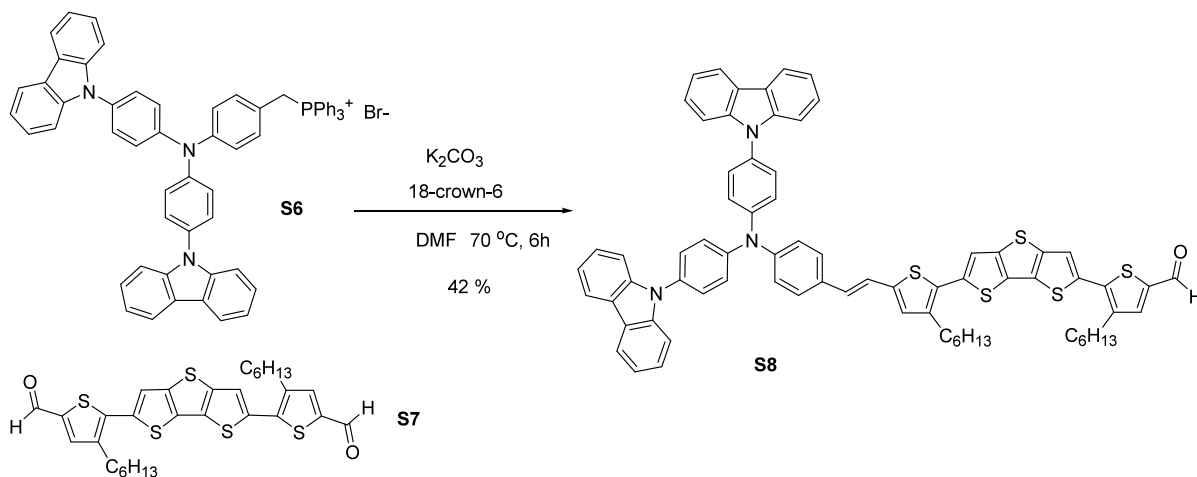
{4-[Bis-(4-carbazol-9-yl-phenyl)-amino]-benzyl}-triphenylphosphonium bromide (**S6**)



The alcohol **S5** (1.5 g, 2.5 mmol) and PPh_3HBr (0.93 g, 2.7 mmol) was dissolved in chloroform (20 mL) and the mixture was heated to reflux for 3h. After the solvent was removed, the residue was triturated with hexane and CH_2Cl_2 and filtered to yield the phosphonium salt **S6** (2.2 g, 2.4 mmol, 94 %) as a pale yellow solid. m.p. 215 °C.

^1H NMR (500 MHz, CDCl_3): δ 5.48 (2 H, d, $J = 13.5$ Hz), 7.07 (2 H, d, $J = 8.5$ Hz), 7.17 (2 H, dd, $J = 11$ Hz, 2.5 Hz), 7.28 (1 H, d, $J = 1.5$ Hz), 7.29 (2 H, t, $J = 1.5$ Hz), 7.31-7.33 (5 H, m), 7.42-7.50 (12 H, m), 7.64-7.68 (6H, m), 7.76-7.84 (9H, m), 8.15 (2 H, dt, $J = 7.5$ Hz, 1.0 Hz), ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 109.61, 117.48, 118.16, 119.87, 120.42, 122.51, 124.23, 124.85, 126.08, 127.96, 129.97, 130.07, 131.68, 132.11, 133.92, 135.00, 140.14, 145.63. m/z (EI) [rel. intensity] 850.3[100, (M)⁺], 851.3[70, (M+H)⁺], 852.3[25, (M+2H)⁺]. m/z (EI): 850.3342 [M]⁺ calcd. for $\text{C}_{61}\text{H}_{45}\text{N}_3\text{P}$ 850.3351. FT-IR (neat cm^{-1}): 3043, 1625, 1599, 1507, 1479, 1452, 1312, 1285, 1230, 1182, 1148, 1118, 1014, 910, 831, 748, 723.

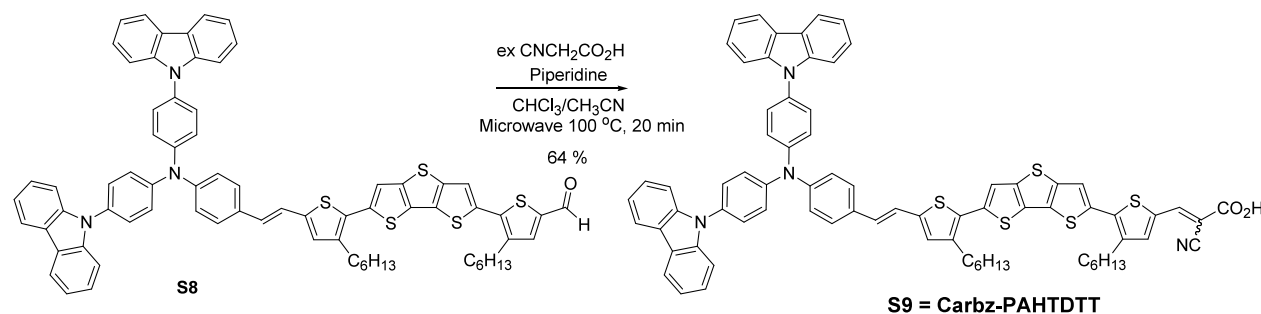
5-{6-[5-(2-{4-[Bis-(4-carbazol-9-yl-phenyl)-amino]-phenyl}-vinyl)-3-hexyl-thien-2-yl]-dithieno[3,2-b;2',3'-d] thiophen -2-yl}-4-hexyl-thien-2-carbaldehyde (**S8**)



To a stirred solution of the aldehyde **S7** (292 mg, 0.50 mmol), anhydrous K_2CO_3 (138 mg, 1 mmol), and 18-crown-6 (7 mg, 0.025 mmol) in DMF (10 mL) at a temperature of 70 °C was added dropwise a solution of the phosphonium salt **S6** (465 mg, 0.50 mmol) in DMF (10 mL) over 3h. The reaction mixture was stirred for a further 3 h at 70 °C. It was then cooled and extracted with CH_2Cl_2 . The combined organic layers were washed with water and brine solution. The organic phase was dried over $MgSO_4$, and purified by column chromatography on silica gel eluting with hexane/dichloromethane (v/v 4/1 to 1/4) to give the alkene **S8** as red solid (241 mg, 0.21 mmol, 42%). $R_f = 0.45$ (1:1 pet. spirit 40-60 / CH_2Cl_2). m. p. 210 °C.

1H NMR (500 MHz, $CDCl_3$): δ 0.92 (6 H, t, $J = 6.5$ Hz), 1.35 (8 H, br m), 1.41-1.47 (4H, br m), 1.68-1.76 (4H, br m), 2.81 (2 H, t, $J = 7.5$ Hz), 2.87 (2 H, t, $J = 8.0$ Hz) 6.94 (1 H, d, $J = 16$ Hz), 6.96 (1 H, s), 7.13 (1 H, d, $J = 16$ Hz), 7.30-7.34 (6H, m), 7.43-7.54 (16H, m), 7.63 (1 H, s), 8.17 (4 H, d, $J = 8.5$ Hz), 9.86. (1 H, s) ^{13}C NMR (125 MHz, $CDCl_3$): 14.06, 14.10, 22.59, 22.62, 29.17, 29.28, 29.45, 29.52, 30.31, 30.47, 31.62, 31.70, 109.79, 118.77, 119.90, 120.33, 120.46, 120.75, 123.31, 124.64, 125.14, 125.91, 125.97, 127.64, 128.11, 128.18, 129.11, 129.35, 130.12, 132.06, 132.26, 132.58, 135.25, 138.24, 138.92, 140.69, 140.79, 140.97, 141.07, 141.31, 141.65, 142.33, 146.33, 146.82, 182.47. m/z (EI) [rel. intensity] 1155.3[100, (M)⁺], 1156.3[95, (M+H)⁺], 1157.3[40, (M+2H)⁺], 1158.3[20, (M+3H)⁺]. m/z (EI): 1155.3419 calcd. for $C_{73}H_{61}N_{43}OS_5$ 1155.3418. FT-IR (neat cm^{-1}): 3043, 2923, 2853, 1665, 1596, 1507, 1479, 1451, 1312, 1287, 1230, 1179, 832, 749, 723, 674.

3-(5-{6-[5-(2-{4-[Bis-(4-carbazol-9-yl-phenyl)-amino]-phenyl)-vinyl]-3-hexyl-thien-2-yl]-dithieno[3,2-b;2',3'-d]thiophen-2-yl}-4-hexyl-thien-2-yl)-2-cyano-acrylic acid (**S9**, Carbz-PAHTDTT)



A solution of the aldehyde **S8** (70 mg, 0.14 mmol) in a mixture of acetonitrile (10 mL) and chloroform (10 mL) with an excess of cyanoacetic acid (102 mg, 1.2 mmol) and piperidine

(0.1 mL) was heated to 100 °C in a microwave reactor for 20 min. The reaction mixture was extracted with CH₂Cl₂ and the combined organic extracts were washed with 1N HCl, water, and brine solution. The organic layer was dried over MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel eluting with dichloromethane / methanol / acetic acid (in the volume proportions 10/1/0 to 10/1/0.1) to give the organic dye **S9** (46 mg, 0.038 mmol, 64%) as dark solid. m.p. 225 °C. R_f = 0.44 (10:1:0.1 CH₂Cl₂/MeOH/AcOH).

¹H NMR (500 MHz, DMSO-d₆/CDCl₃ (v/v = 1/1): δ 0.84 (6 H, t, *J* = 6.5 Hz), 1.27 (8 H, br m), 1.33-1.40 (4H, br m), 1.61-1.68 (4H, br m), 2.75 (2 H, t, *J* = 7.0 Hz), 2.83 (2 H, t, *J* = 7.5 Hz) 6.88 (1 H, d, *J* = 16 Hz), 7.00 (1 H, s), 7.17 (1 H, d, *J* = 16 Hz), 7.22-7.26 (6H, m), 7.37-7.45 (13H, m), 7.50-7.53 (5H, m), 7.66 (1 H, s), 7.71 (1 H, s), 8.11 (8 H, d, *J* = 8.0 Hz), 8.28. (1 H, s)

¹³C NMR (125 MHz, DMSO-d₆/CDCl₃ (v/v=1/1) at 40 °C): 13.40, 13.42, 21.68, 21.72, 28.18, 28.31, 28.34, 28.63, 29.24, 29.54, 30.72, 30.78, 98.61, 109.26, 115.65, 118.54, 119.36, 119.66, 119.83, 120.78, 122.35, 123.92, 124.58, 124.63, 125.45, 127.20, 127.39, 127.57, 128.11, 128.94, 128.99, 131.00, 131.49, 131.58, 132.89, 134.20, 137.31, 139.63, 140.11, 140.32, 140.90, 141.27, 142.18, 145.06, 145.62, 146.02, 163.15; *m/z* (EI) [rel. intensity] 1222.3.[80, (M)⁺], 1223.3[100, (M+H)⁺], 1224.3[50, (M+2H)⁺], 1224.3[25, (M+3H)⁺]. *m/z* (EI): 1222.3476 calcd. for C₇₆H₆₂N₄O₂S₅1222.3476. FT-IR (neat cm⁻¹):3042, 2926, 2856, 1683, 1570, 1506, 1479, 1452, 1392, 1312, 1273, 1229, 1173, 1106, 1014, 938, 830, 749, 723.

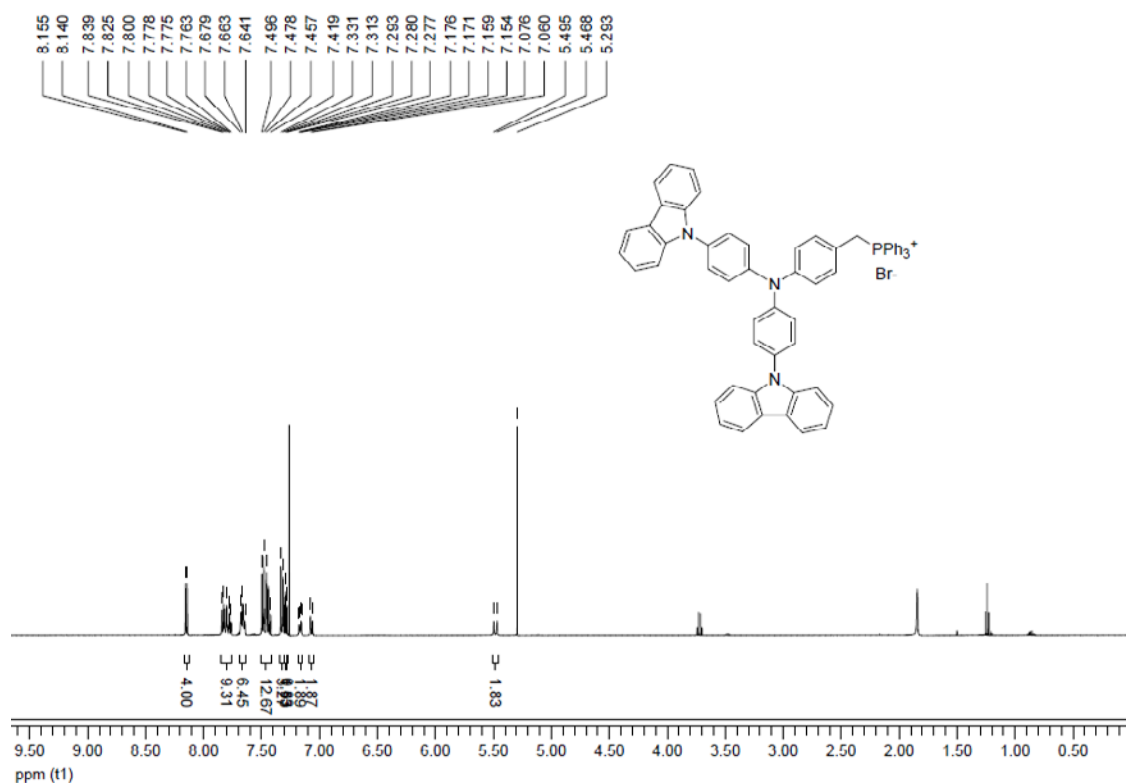


Figure S4: ^1H NMR spectrum of **S6** (500 MHz, CDCl_3).

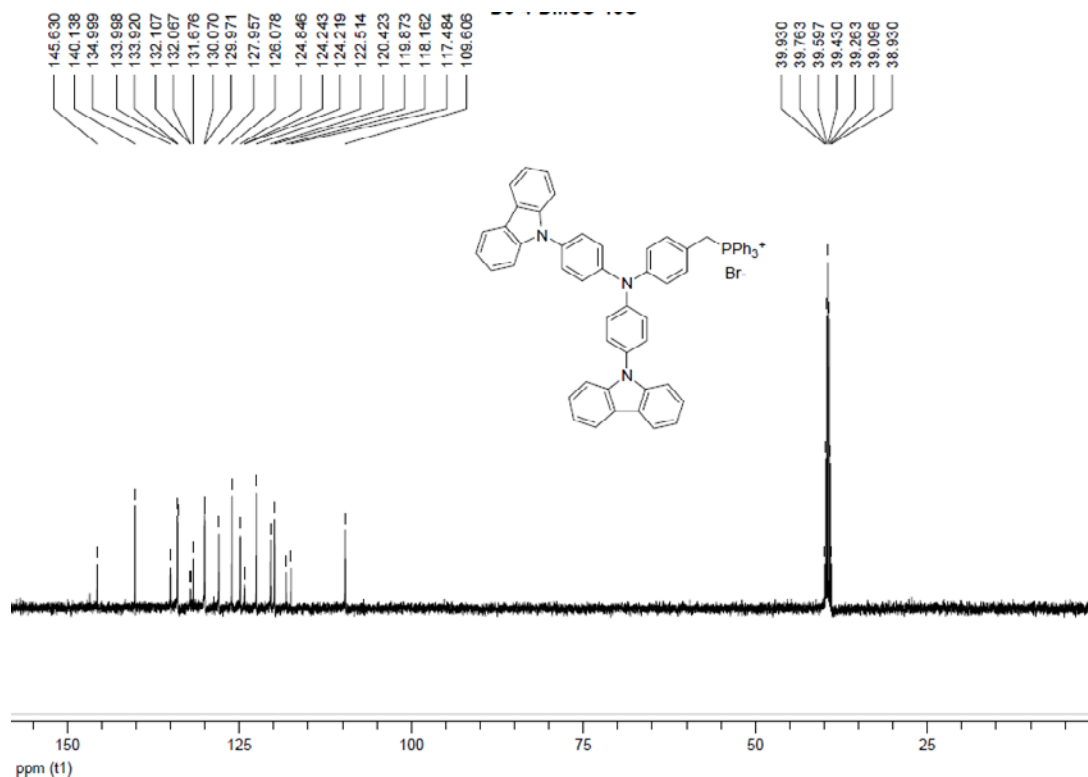


Figure S5: ^{13}C NMR spectrum of **S6** (125 MHz, $\text{DMSO}-d_6$).

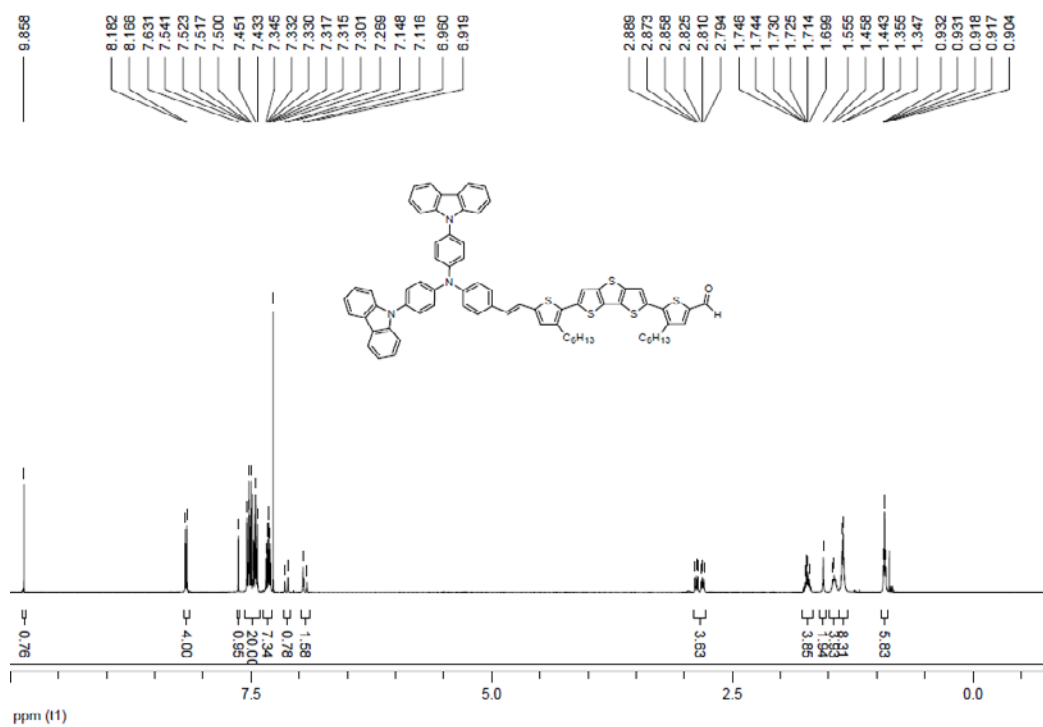


Figure S6: ¹H NMR spectrum of S8 (500 MHz, CDCl₃).

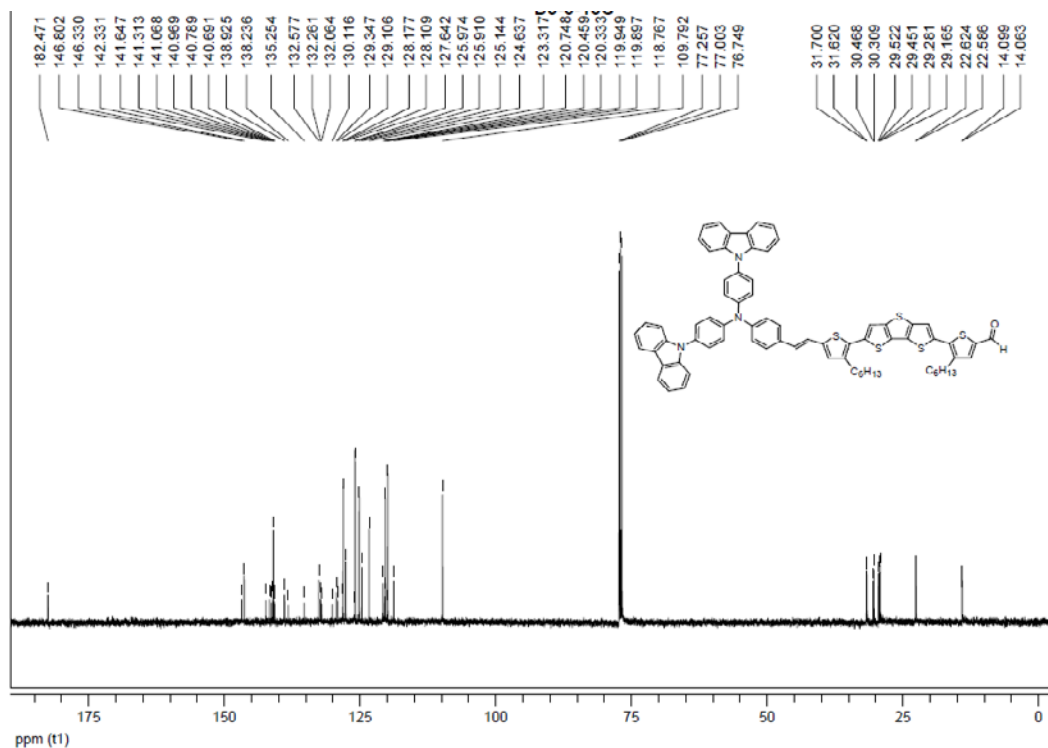


Figure S7: ¹³C NMR spectrum of S8 (125 MHz, CDCl₃).

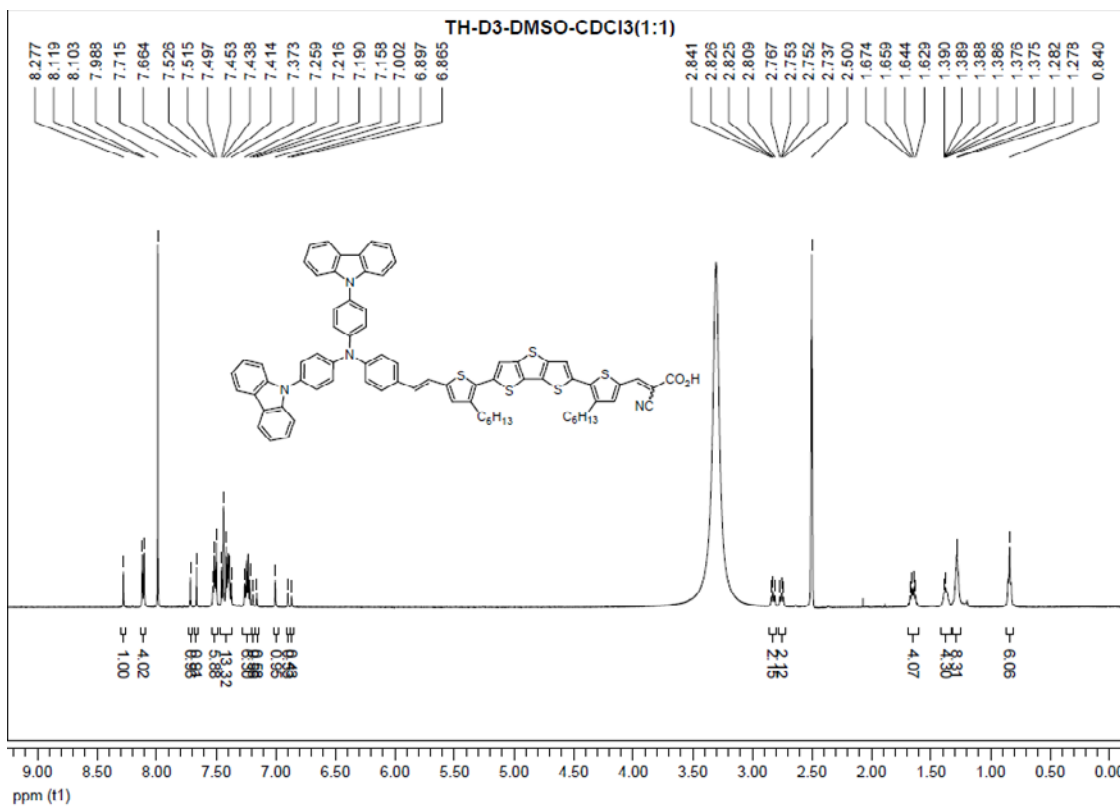


Figure S8: ¹H NMR spectrum of S9 (Carbz-PAHTDTT, 500 MHz, DMSO-*d*₆:CDCl₃ (v/v=1:1)).

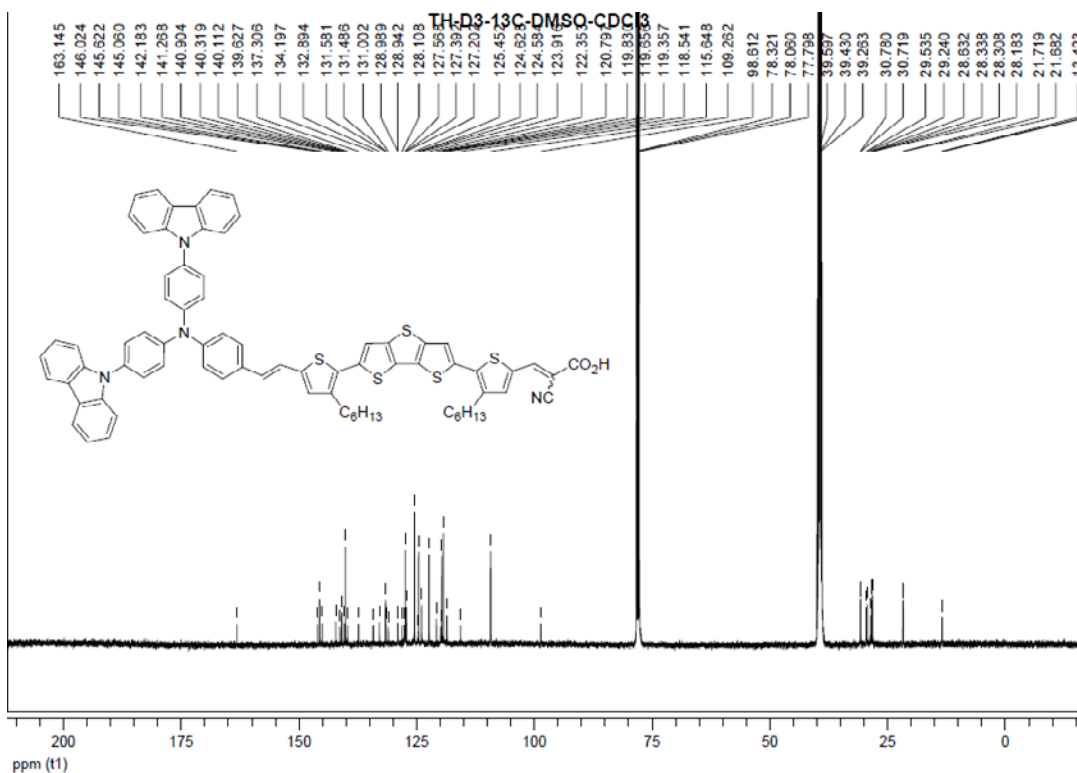


Figure S9: ¹³C NMR spectrum of S9 (Carbz-PAHTDTT, 500 MHz, DMSO-*d*₆:CDCl₃ (v/v=1:1)).

Photophysical and Electrochemical Data for Carbz-PAHTDTT (S9)

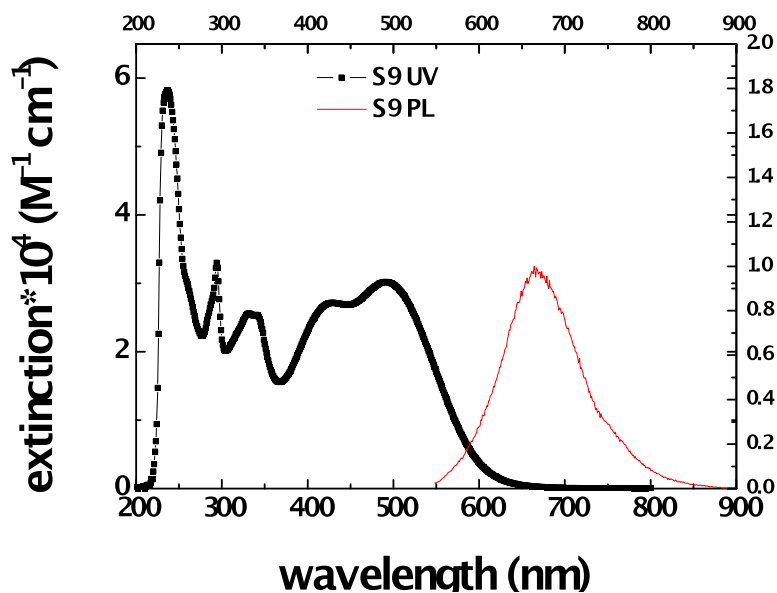


Figure S10: UV-Vis and photoluminescence spectra for **S9 (Carbz-PAHTDTT)**, measured as a 0.02 mM solution in CH_2Cl_2

Table S3. Summary of Electrochemical and Photophysical Data for **S9 (Carbz-PAHTDTT)**.

	Abs ($\epsilon \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1}$) ^a	PL (λ_{max}) ^a	E_{ox} (V) vs (NHE) ^b	E_{0-0} (V) vs (Abs/Em) ^c	$E_{\text{ox}} - E_{0-0}$ (V) vs (NHE)
S9	235(1.7), 294 (3.3), 330 (2.5), 426 (2.7), 491 (3.0)	664	0.91	2.11	-1.20

^a 0.02 mM CH_2Cl_2 solution at 298 K. ^b Cyclic voltammogram of the onset point of the dyes were measured in dry CH_2Cl_2 containing 0.1 M TBAPF₆ (tetrabutylammonium hexafluorophosphate) as supporting electrolyte, Ag/AgCl as a reference electrode, and glassy carbon as working electrode. Potentials calibrated with Fc⁺/Fc were converted normal hydrogen electrode (NHE) by addition of +0.63 V. ^cThe E_{0-0} transition energy was estimated from the intersection of the absorption and emission spectra, using the following equation $x \text{ V} = 10^7 / (\lambda_{\text{intersection}} \text{ nm} \times 8065.48 \text{ cm}^{-1})$