Supporting Information

Efficient solution processed non-doped red emitter based on carbazole-triphenylamine end-capped di(thiophen-2-yl)benzothiadiazole for pure red organic light-emitting diode

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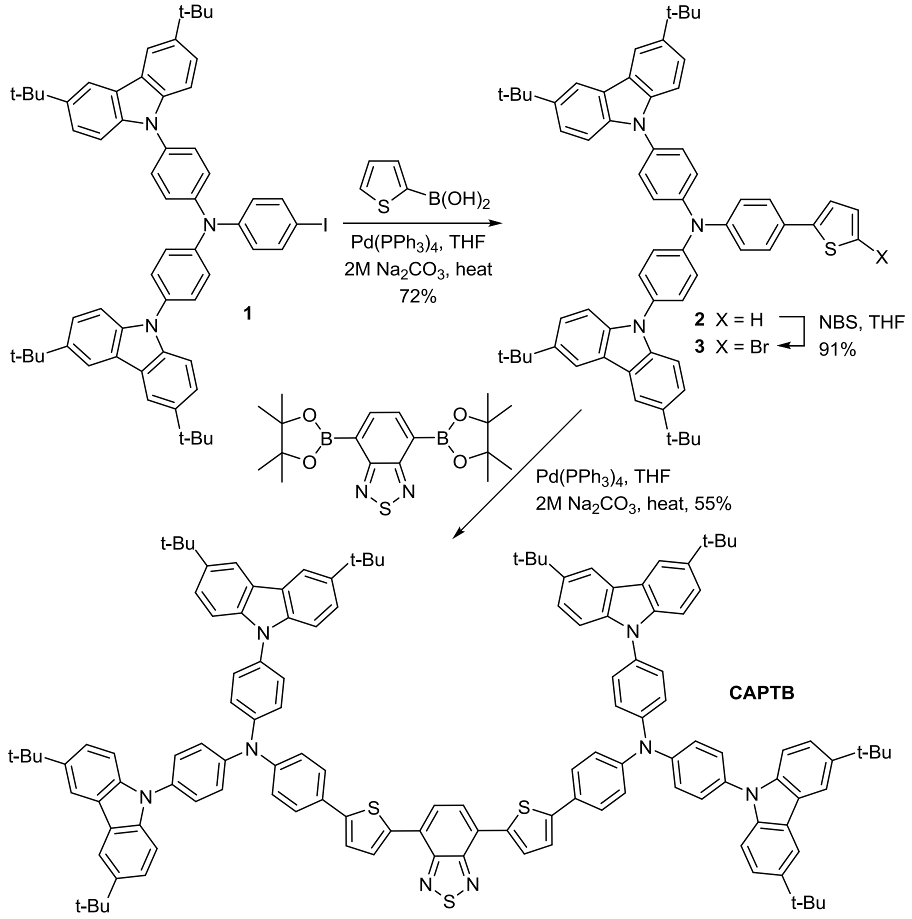
1. General Procedures

All reagents were purchased from Aldrich, Acros or Fluka and used without further purification. All solvents were supplied by Thai companies and used without further distillation. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and distilled. Dichloromethane for cyclic voltammetry (CV) measurements was washed with conc. H_2SO_4 and distilled twice from calcium hydride. Chromatographic separations were carried out on silica gel Merk Silica gel 60 (0.0630-0.200 mm).

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Brüker AVANCE 300 MHz spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ as solvent in all cases. Infrared (IR) spectra were measured on a Perkin-Elmer FTIR spectroscopy spectrum RXI spectrometer as KBr disc. Ultraviolet-visible (UV-Vis) spectra were recorded as a diluted solution in spectroscopic grade dichloromethane on a Perkin-Elmer UV Lambda 25 spectrometer. Photoluminescence spectra and the fluorescence quantum yields (Φ_F) were recorded with a Perkin-Elmer LS 50B Luminescence Spectrometer as a dilute solution in spectroscopic grade dichloromethane and thin film obtained by spin casting. The fluorescence quantum yields (Φ_F) were determined by comparison with a fluorescence standard of coumarin 6 in ethanol + 0.01% HCl (Φ_F = 0.78).[1] Differential scanning carolimetry (DSC) analysis and thermogravimetry analysis (TGA) were performed on a METTLER DSC823e thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer, respectively, with heating rate of 10 ^{o}C/min under nitrogen atmosphere. Cyclic voltammetry (CV) measurements were carried out on an Autolab potentiostat PGSTAT 12 with a three electrode system (platinum counter electrode, glassy carbon working electrode and Ag/Ag$^+$ reference electrode) at scan rate of 50 mV/s in dichloromethane under argon atmosphere. The concentration of analytical materials and tetrabutyl ammonium hexafluorophosphate (n-Bu_4NPF_6) were 10^{-3} M and 0.1 M, respectively. Melting points were measured using an Electrothermal IA 9100 series of digital melting point instrument and are uncorrected. High resolution mass spectrometry (HRMS) analysis was performed by Mass Spectrometry Unit, Mahidol University, Thailand. The atomic force microscopy (AFM) analysis was performed on Park System model XE 100 using standard non contact mode with resonance of 316.17 KHz at Ubon Ratchathani University.

2. Synthesis and Characterization

The synthesis of **CAPTB** is outlined in Scheme S1.



Scheme S1. Synthetic route to **CAPTB**

***N,N*-bis(4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl)-4-iodoaniline (1):** A mixture of tris(4-iodophenyl)amine (3.0 g, 4.8 mmol), 3,6-di-tert-butylcarbazole (2.7 g, 9.6 mmol), CuI (0.9 g, 4.8 mmol), K_3PO_4 (3.3 g, 24.1 mmol), and ±*trans*-1,2-diaminocyclohexane (0.6 ml, 4.8 mmol) in toluene (60 ml) was degassed with N_2 for 5 min and then heated at reflux under N_2 atmosphere for 24 h. After cooling, the solid residue was filtered out and washed with CH_2Cl_2 (50 ml). The organic filtrate was washed with water (100 ml x 2) and brine solution (100 ml), dried over anhydrous Na_2SO_4 and evaporated to dryness. Purification by silica gel column chromatography using CH_2Cl_2/hexane (1:9) as eluent gave light gray solids (1.9 g, 44%). m.p. >250 ^{o}C, FT-IR (KBr, ν, cm^{-1}): 3042, 2955, 1507, 1483, 1312, 1295, 1262, 810. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.37 (4H, s), 7.80 (2H, d, *J* = 7.2 Hz), 7.50-7.68 (16H, m), 7.20 (2H, d, *J* = 7.2 Hz), 1.67 (36H, s). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 147.2, 145.9, 145.6, 142.6, 139.4, 133.3, 130.9, 128.7, 127.8, 126.8, 125.3, 124.5, 123.6, 123.3, 122.7, 116.3, 110.8, 109.2, 34.8, 32.0. HRMS calcd for $C_{58}H_{60}IN_3$: *m/z* 925.3832; found: *m/z* 926.3902 [MH$^+$].

***N,N*-bis(4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl)-4-(thiophen-2-yl)aniline (2):** A mixture of **1** (2.0 g, 1.9 mmol), 2-thiopheneboronic acid (0.27 g, 1.9 mmol), $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol), 2 M Na_2CO_3 aqueous (16 ml) in THF (40 ml) was degassed with N_2 for 5 min and then heated at reflux under N_2 atmosphere for 24 h. After cooling, CH_2Cl_2 (100 ml) was added and the organic layer was washed with water (100 ml x 2) and brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. Purification by silica gel column chromatography using CH_2Cl_2/hexane (1:9) as eluent gave light yellow solids (1.3 g, 72%). m.p. >250 ^{o}C, FT-IR (KBr, ν, cm^{-1}): 3041, 2958, 1507, 1473, 1316, 1294, 1262, 809. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.11 (4H, d, *J* = 5.4 Hz), 7.59 (2H, s), 7.24-7.48 (20H, m), 7.05 (1H, s), 1.40 (36H, s). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 146.6, 145.9, 143.6, 142.7, 139.1, 132.7, 129.5, 128.5, 127.7, 121.1, 125.2, 124.9, 123.8, 123.1, 116.5, 109.5, 34.8, 32.2. HRMS calcd for $C_{62}H_{63}N_3S$: *m/z* 881.4743; found: *m/z* 882.4819 [MH^+].

4-(5-Bromothiophen-2-yl)-*N*,*N*-bis(4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl)aniline (3): *N*-Bromosuccinimide (0.35 g, 2.0 mmol) was added in small portions to a solution of **2** (1.7 g, 1.9 mmol) in THF (30 ml). The mixture was stirred at room temperature under N_2 for a further 1 h. Water (30 ml) and CH_2Cl_2 (100 ml) were added. The organic phase was separated, washed with water (100 ml x 2), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents were removed to dryness. Purification by silica gel column chromatography eluting with CH_2Cl_2/hexane (1:9) gave brominated product as light yellow solids (1.5 g, 91%). m.p. >250 °C, FT-IR (KBr, ν, cm^{-1}): 3041, 2959, 1507, 1316, 1294, 1263, 809. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.15 (4H, d, *J* = 1.2 Hz), 7.26-7.52 (21H, m), 7.03 (1H, s), 1.48 (36H, s). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 147.3, 145.7, 142.9, 139.3, 138.5, 133.4, 127.7, 126.2, 125.2, 123.6, 123.3, 116.3, 109.2, 86.3, 34.7, 32.0. HRMS calcd for $C_{62}H_{62}BrN_3S$: *m/z* 959.3848; found: *m/z* 960.3908 [MH^+].

Synthesis of 4,7-Bis{5-(N,N-bis[4-(3,6-di-tert-butylcarbazol-N-yl)phenyl]aminophenyl)-thien-2-yl}-2,1,3-benzothiadiazole (CAPTB)

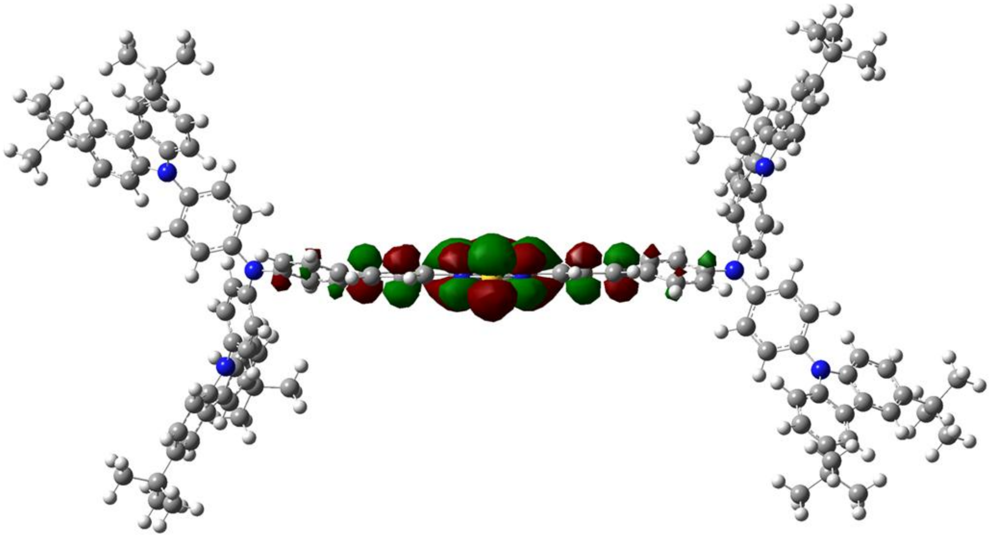
Compound **CAPTB** was prepared from **3** and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole with a method similarly to that described above for **2** and obtained as dark red solid (0.19 g, 55%). m.p. >250 °C; FT-IR (KBr, ν, cm^{-1}): 2958 (C-H), 1505 (C=C), 1474, 1261, 814, 793. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.17 (8H, s), 7.90 (2H, s), 7.71 (4H, d, *J* = 8.2 Hz), 7.40-7.55 (36H, m), 7.32 (4H, d, *J* = 8.2 Hz), 1.49 (72H, s). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 152.6, 147.1, 145.9, 145.2, 142.8, 139.4, 133.2, 129.1, 128.7, 127.8, 127.0, 125.4, 125.2, 124.4, 123.9, 123.3, 123.3, 116.2, 109.2, 34.7, 32.0. HRMS calcd for $C_{130}H_{126}N_8S_3$: *m/z* 1894.9268; found: *m/z* 1895.5778 [MH^+].

2. Computer quantum calculation results

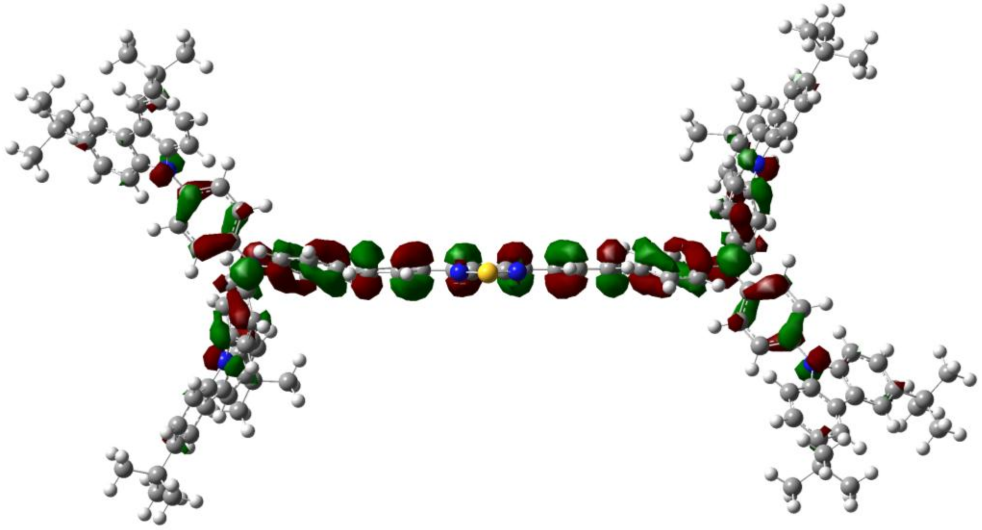
The ground state geometries of **CAPTB** were fully optimized using density functional theory (DFT) at the B3LYP/6-31G (d,p) level, as implemented in Gaussian 03.[2] TDDFT/B3LYP calculation of lowest excitation energies were performed at the optimized geometries of the ground states.

3. Device fabrication and testing

All red OLED devices using **CAPTB** as a non-doped red emissive layer (EML) with the device configurations of ITO/PEDOT:PSS/**CAPTB** (spin-coating)/LiF(0.5 nm):Al(150 nm) and ITO/PEDOT:PSS/**CAPTB** (spin-coating)/BCP(40 nm)/LiF(0.5 nm)/Al(150 nm) were fabricated and characterized as followed. The patterned indium tin oxide (ITO) glass substrate with a sheet resistance 14 Ω/☐ (purchased from Kintec Company) was thoroughly cleaned by successive ultrasonic treatment in detergent, deionised water, isopropanol, and acetone, and then dried at 60 °C in a vacuum oven. A 50 nm thick PEDOT:PSS hole injection layer was spin-coated on top of ITO from a 0.75 wt.% dispersion in water at a spin speed of 3000 rpm for 20 s and dried at 200 °C for 15 min under vacuum. Thin film of **CAPTB** was deposited on top of PEDOT:PSS layer by spin-coating chloroform:toluene solution (5:1) of **CAPTB** (1.5% w/v) on an ITO glass substrate at a spin speed of 3000 rpm for 30 second to get a 30-40 nm thick of hole-transporting layer (HTL). The film thickness was measured by using a Tencor α-Step 500 surface profiler. For double layer device, then BCP was deposited onto the surface of the **CAPTB** film as electron-transporting layer (ETL) with a thickness of 40 nm by evaporation from resistively heated alumina crucibles at evaporation rate of 0.5-1.0 nm/s in vacuum evaporator deposition (ES280, ANS Technology) under a base pressure of ~10^{-5} mbar. The film thickness was monitored and recorded by quartz oscillator thickness meter (TM-350, MAXTEK). The chamber was vented with dry air to load the cathode materials and pumped back; a 0.5 nm thick LiF and a 150 nm thick aluminum (Al) layers were the subsequently deposited through a shadow mask on the top of EML or BCP films without braking vacuum to from an active diode areas of 4 mm^2. The measurement of device efficiency was performed according to M.E. Thomson's protocol and the device external quantum efficiencies were calculated using procedure reported previously.[3] Current density-voltage-luminescence (*J*-*V*-*L*) characteristics were measured simultaneous by the use of a Keithley 2400 source meter and a Newport 1835C power meter equipped with a Newport 818-UV/CM calibrated silicon photodiode. The EL spectra were acquired by an Ocean Optics USB4000 multichannel spectrometer. All the measurements were performed under ambient atmosphere at room temperature soon after breaking the chamber.



LUMO



HOMO

Figure S1 The optimized geometry and HOMO-LUMO orbitals of **CAPTB** calculated using TDDFT/B3LYP/6-31G (d,p) method.

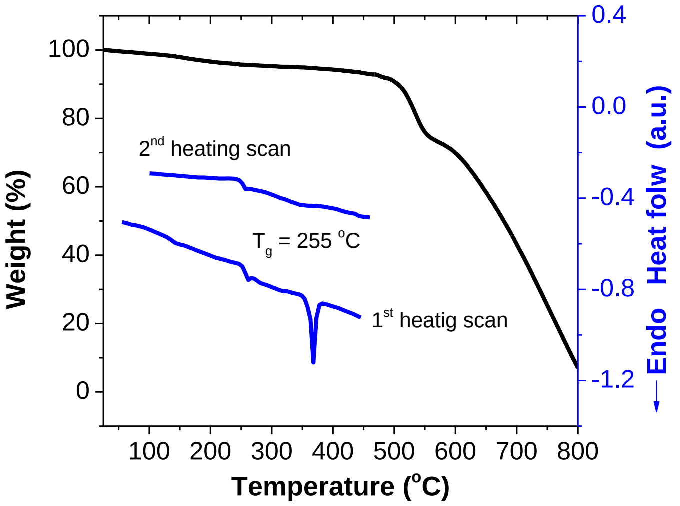
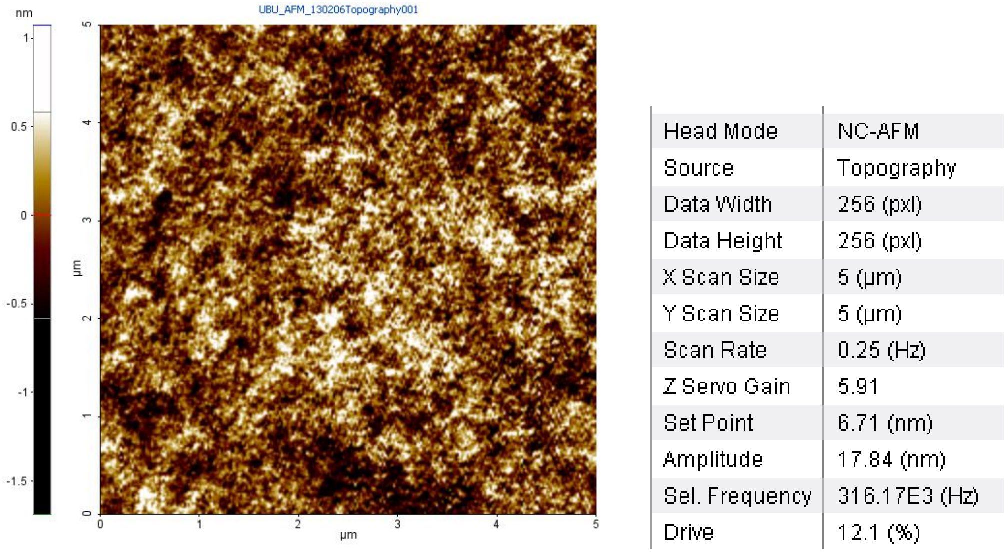


Figure S2 DSC (1st and 2nd heating scan) and TGA curves measured at 10 °C/min under N_2.



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Source	Topography
Data Width	256 (pxl)
Data Height	256 (pxl)
X Scan Size	5 (µm)
Y Scan Size	5 (µm)
Scan Rate	0.25 (Hz)
Z Servo Gain	5.91
Set Point	6.71 (nm)
Amplitude	17.84 (nm)
Sel. Frequency	316.17E3 (Hz)
Drive	12.1 (%)

Figure S3 Tapping mode AFM image of spin-coated film.

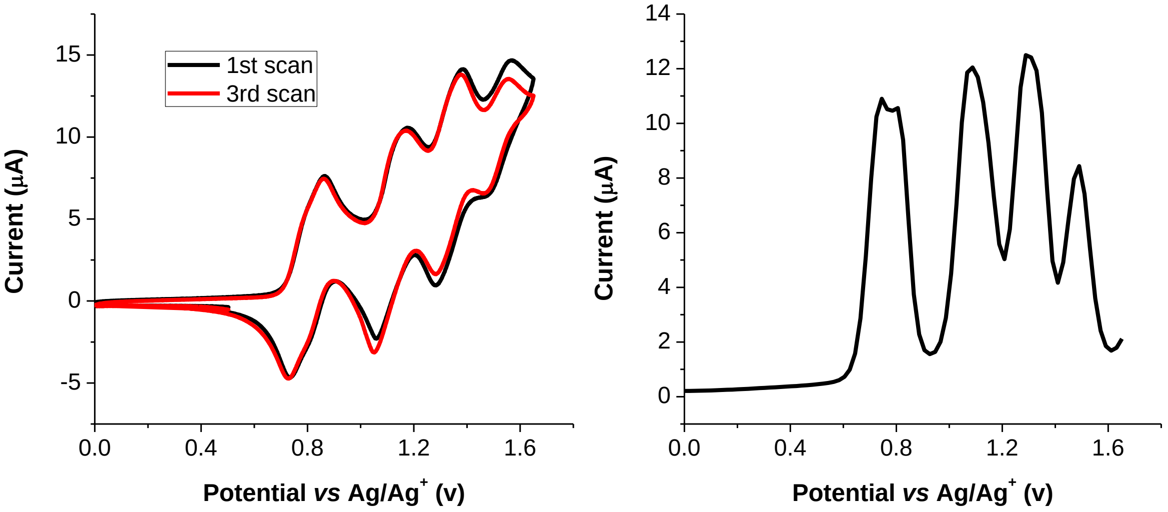

Figure S4 (a) CV and (b) DPV curves of **CAPTB** measured in CH_2Cl_2 at a scan rate of 50 mV/s.

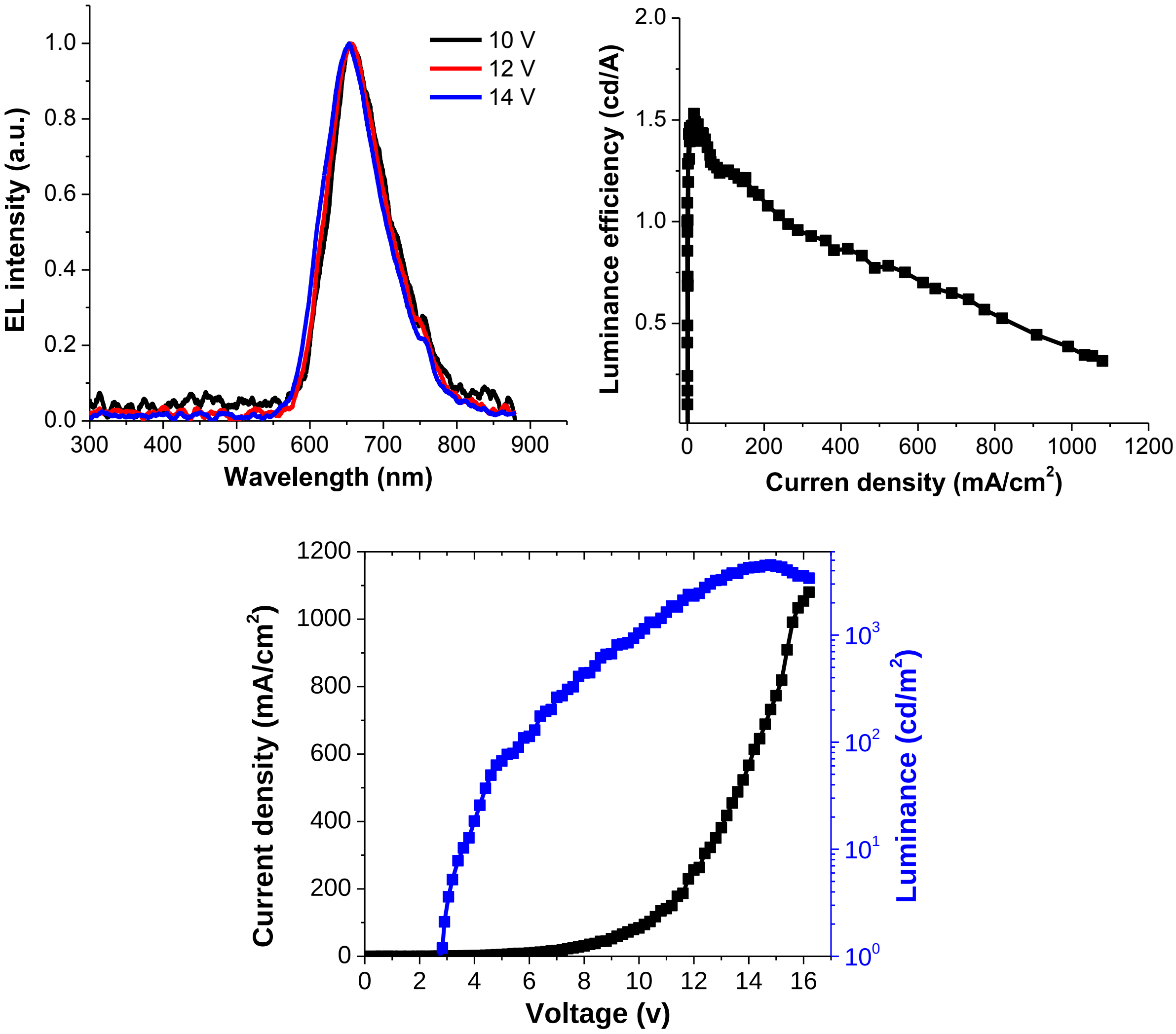

Figure S5 (a) Normalized EL spectra at different applied voltages, (b) Variation of luminance efficiency with current density and (c) *J-V-L* characteristics of **the single layer OLED**.

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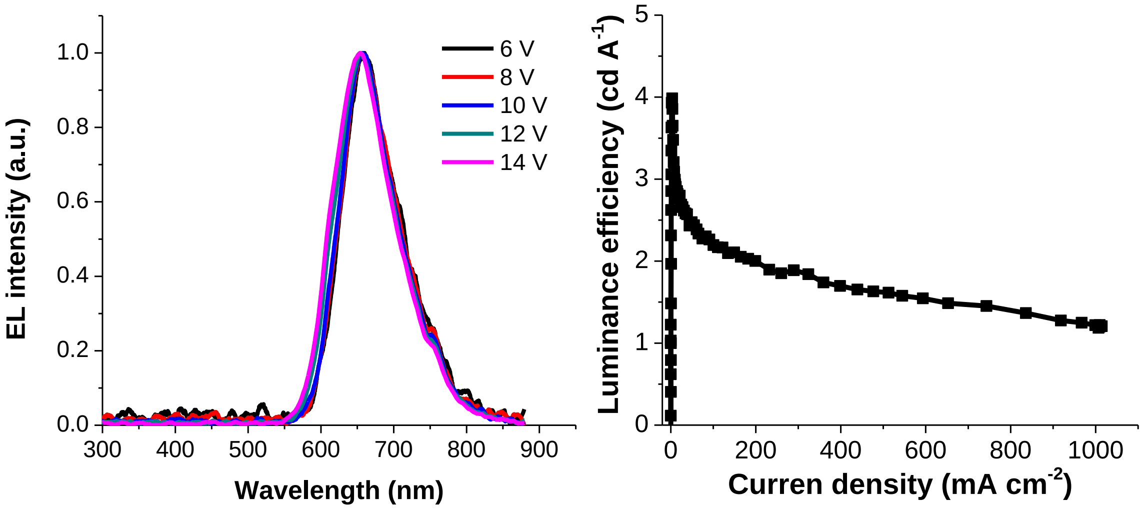


Figure S6 (a) Normalized EL spectra at different applied voltages and (b) Variation of luminance efficiency with current density of **the double layer OLED**.

References

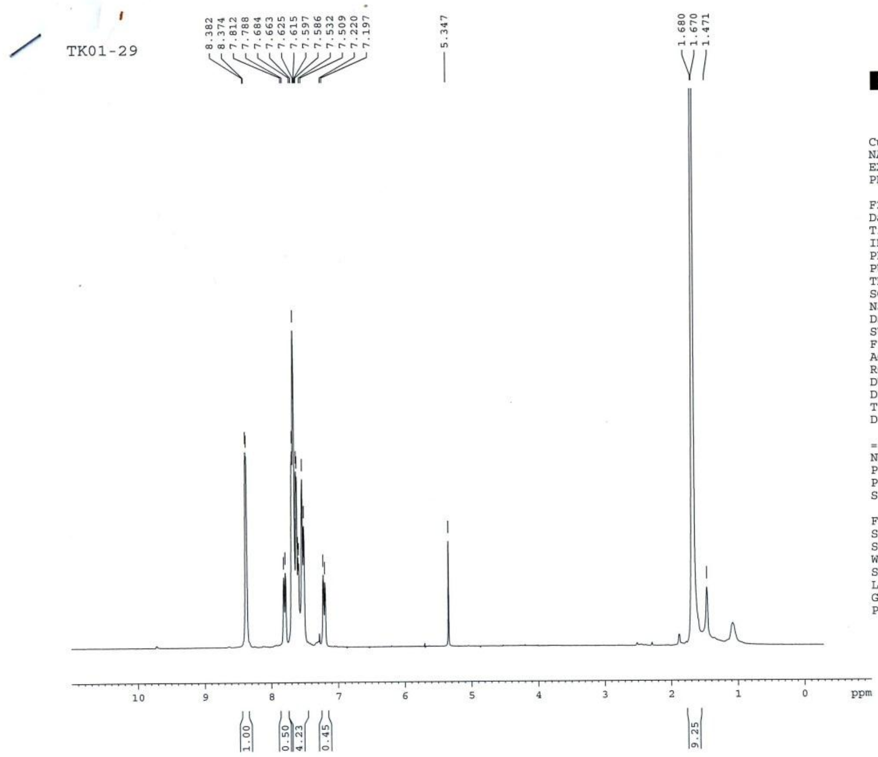
1 T. Kartens, K. Kobs, *J. Phys. Chem.*, 1980, **84**, 1871-1872.

2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision A.1*, Gaussian, Inc., Wallingford CT, **2009**.

3 S. R. Forrest, D. D. C. Bradley, M. E. Thomson, *Adv. Mater.*, 2003, **15**, 1043-1048.

Compound 1

3



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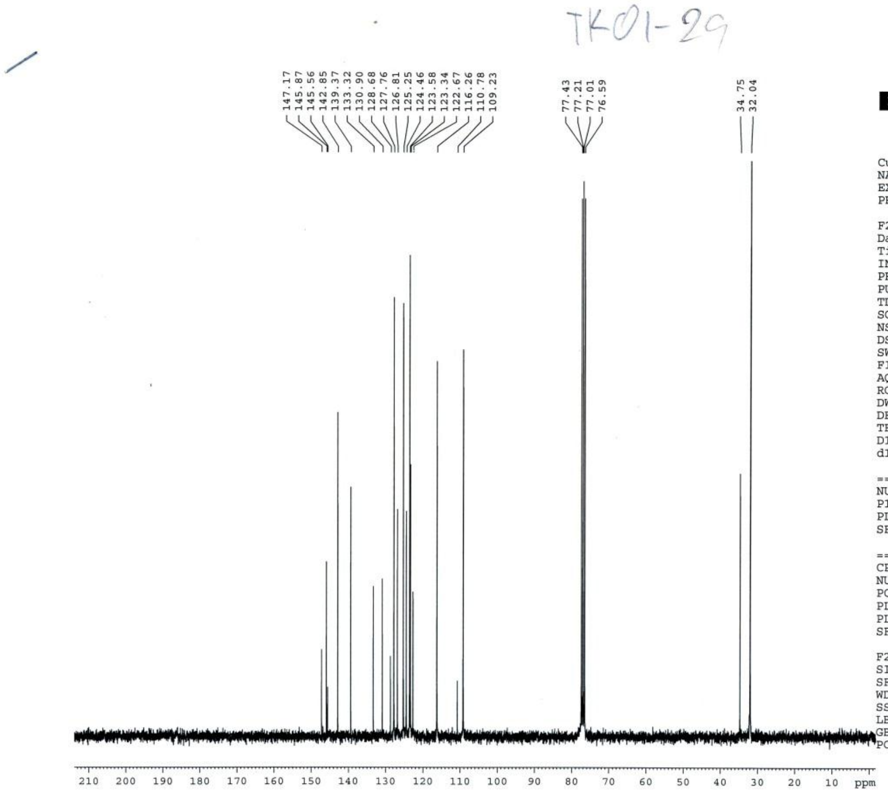

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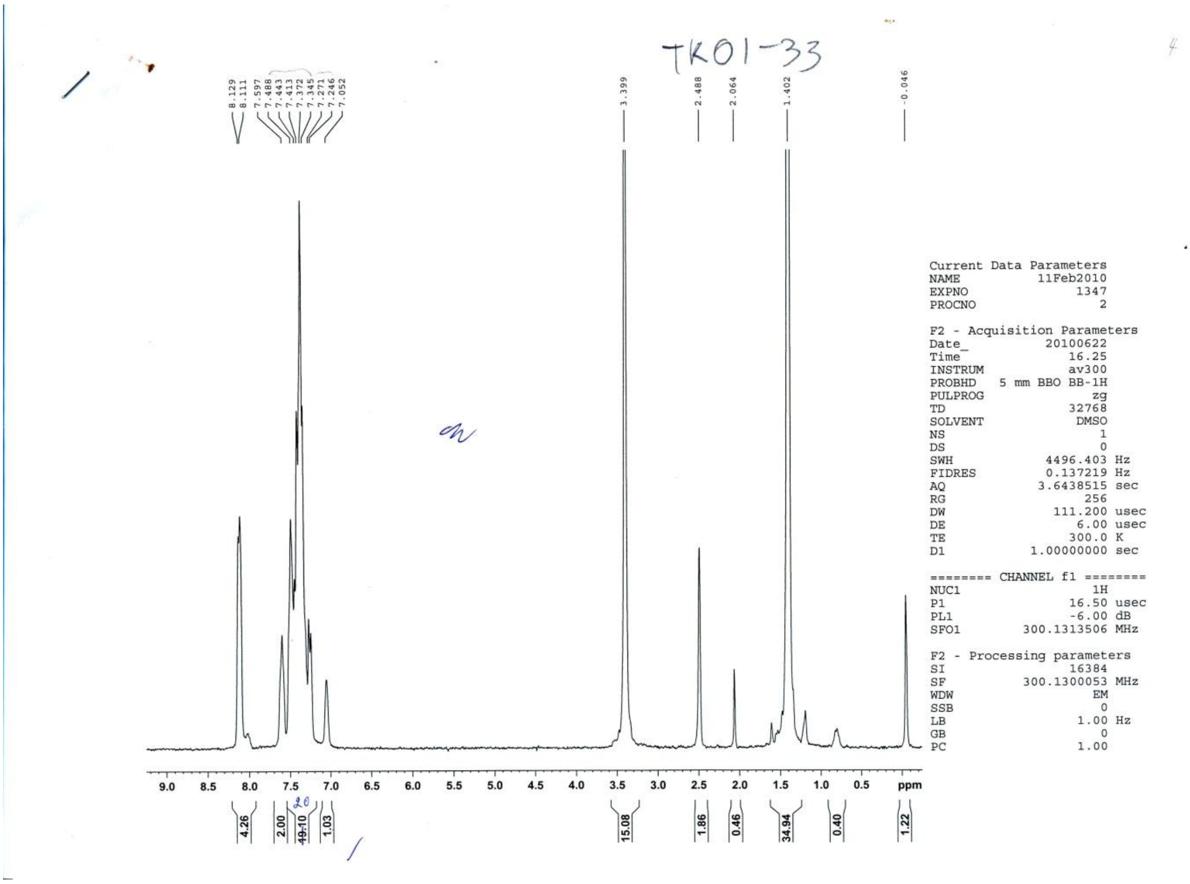
Compound 2



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D1             1.00000000 sec

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PL1                 -6.00 dB
SFO1          300.1313506 MHz

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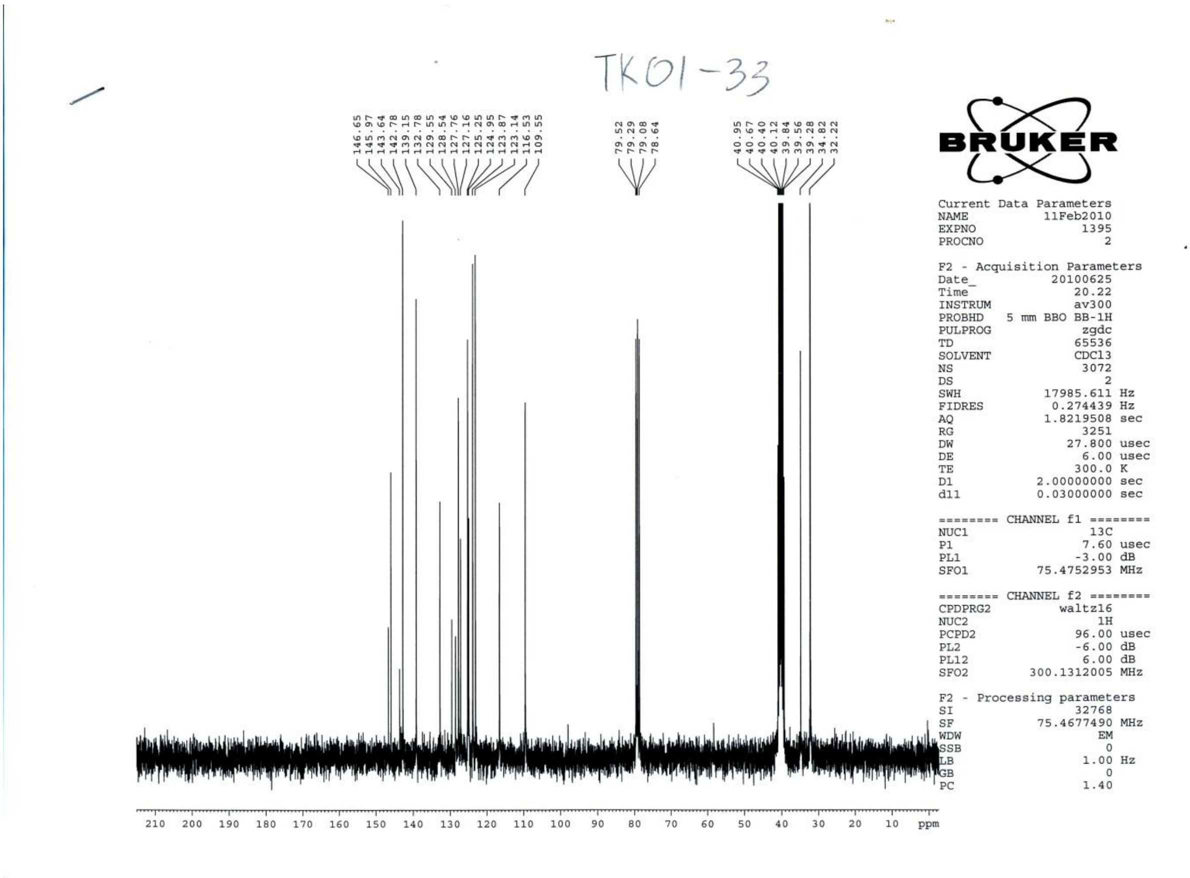

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DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.60 usec
PL1                 -3.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               96.00 usec
PL2                 -6.00 dB
PL12                 6.00 dB
SFO2          300.1312005 MHz

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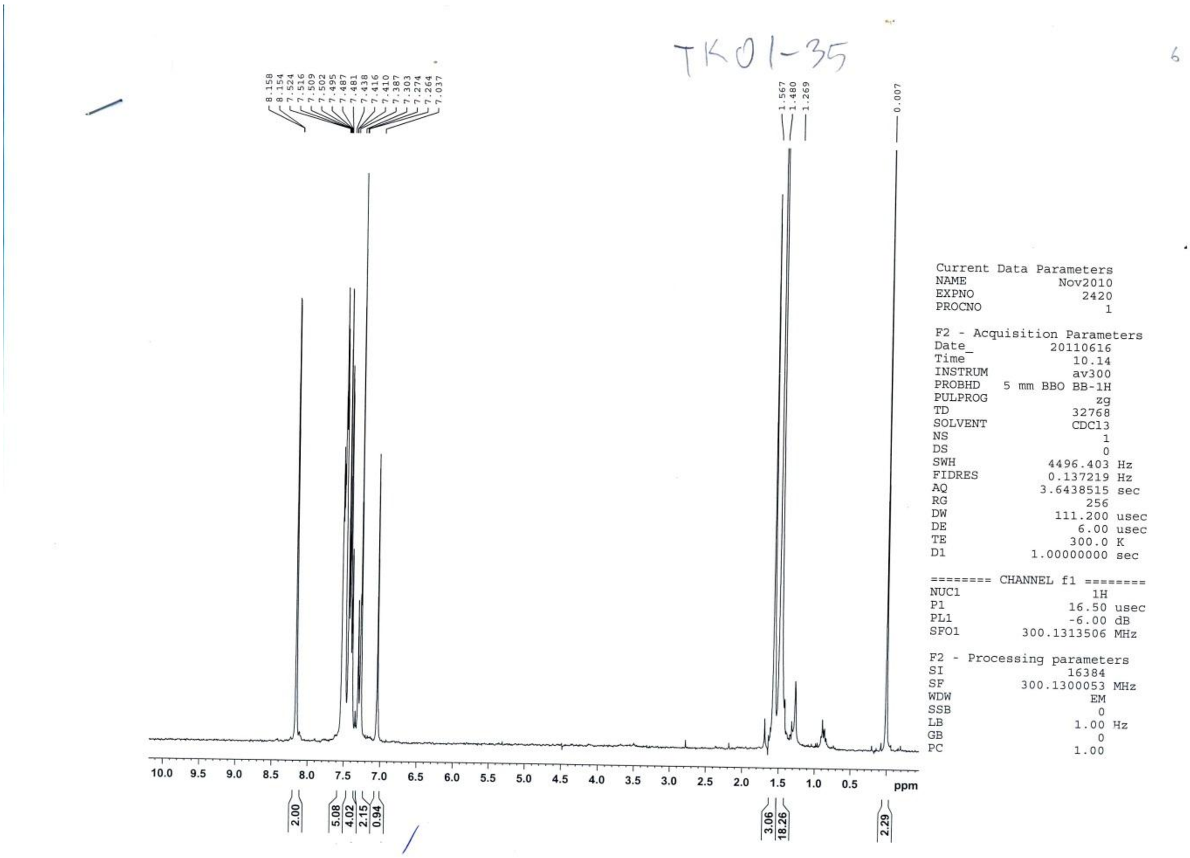
Compound 3



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DE                   6.00 usec
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PL1                 -6.00 dB
SFO1          300.1313506 MHz

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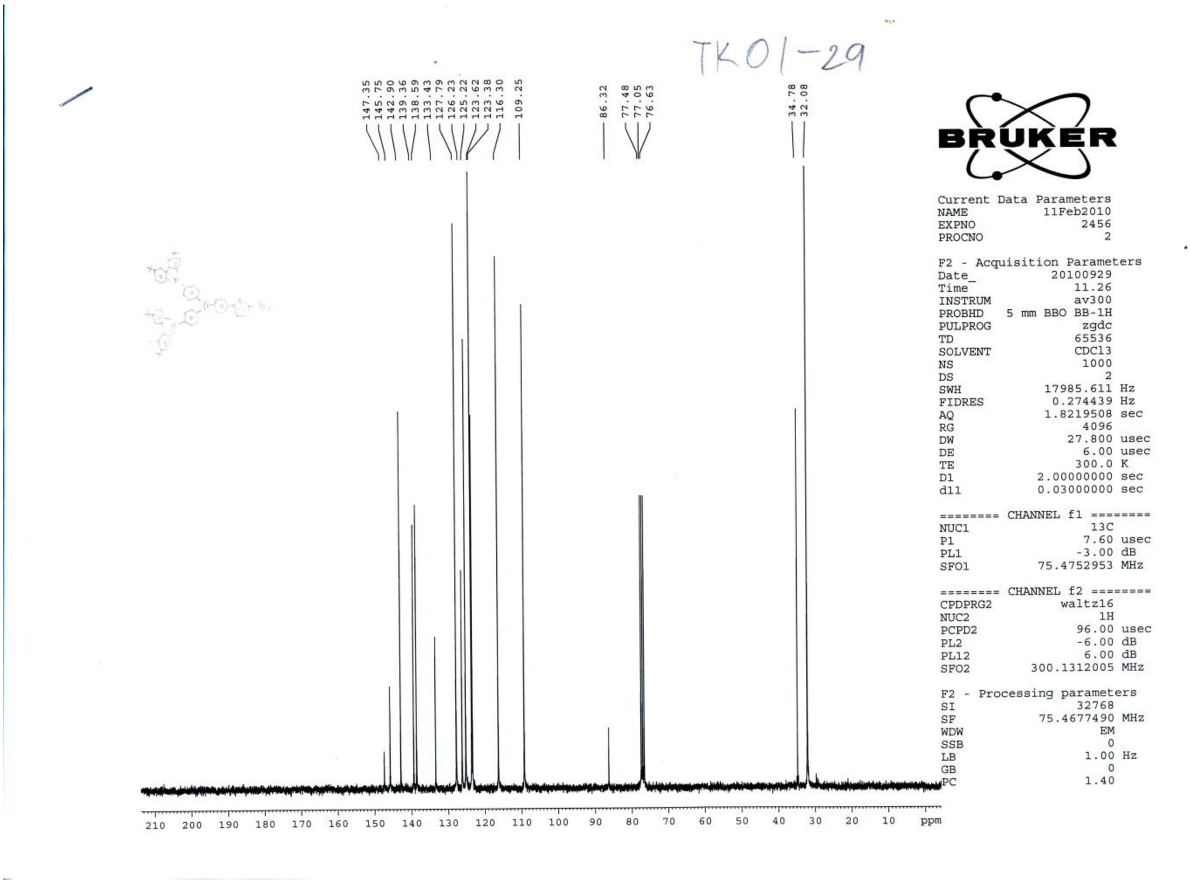

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FIDRES           0.274439 Hz
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RG                   4096
DW                 27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.60 usec
PL1                 -3.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               96.00 usec
PL2                 -6.00 dB
PL12                 6.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
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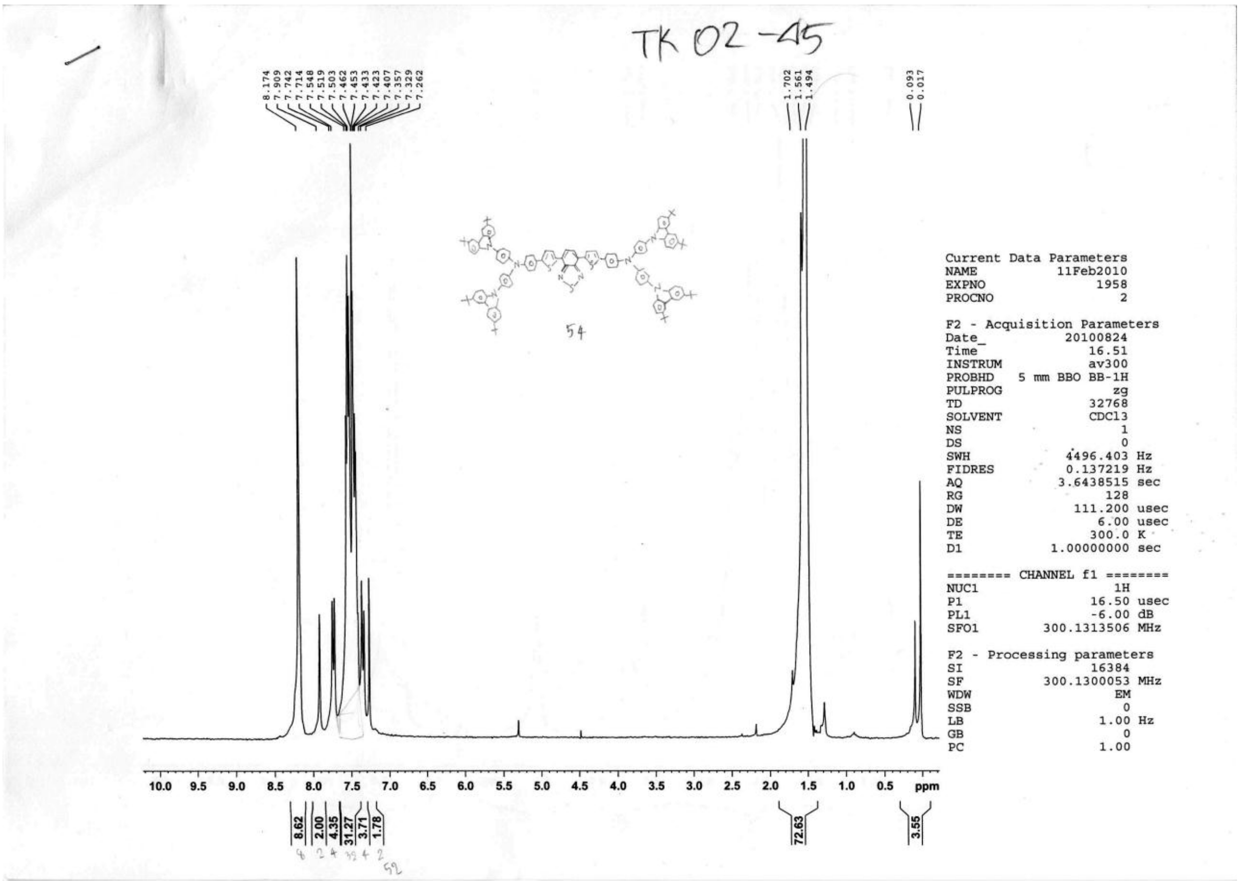
Compound CAPTB



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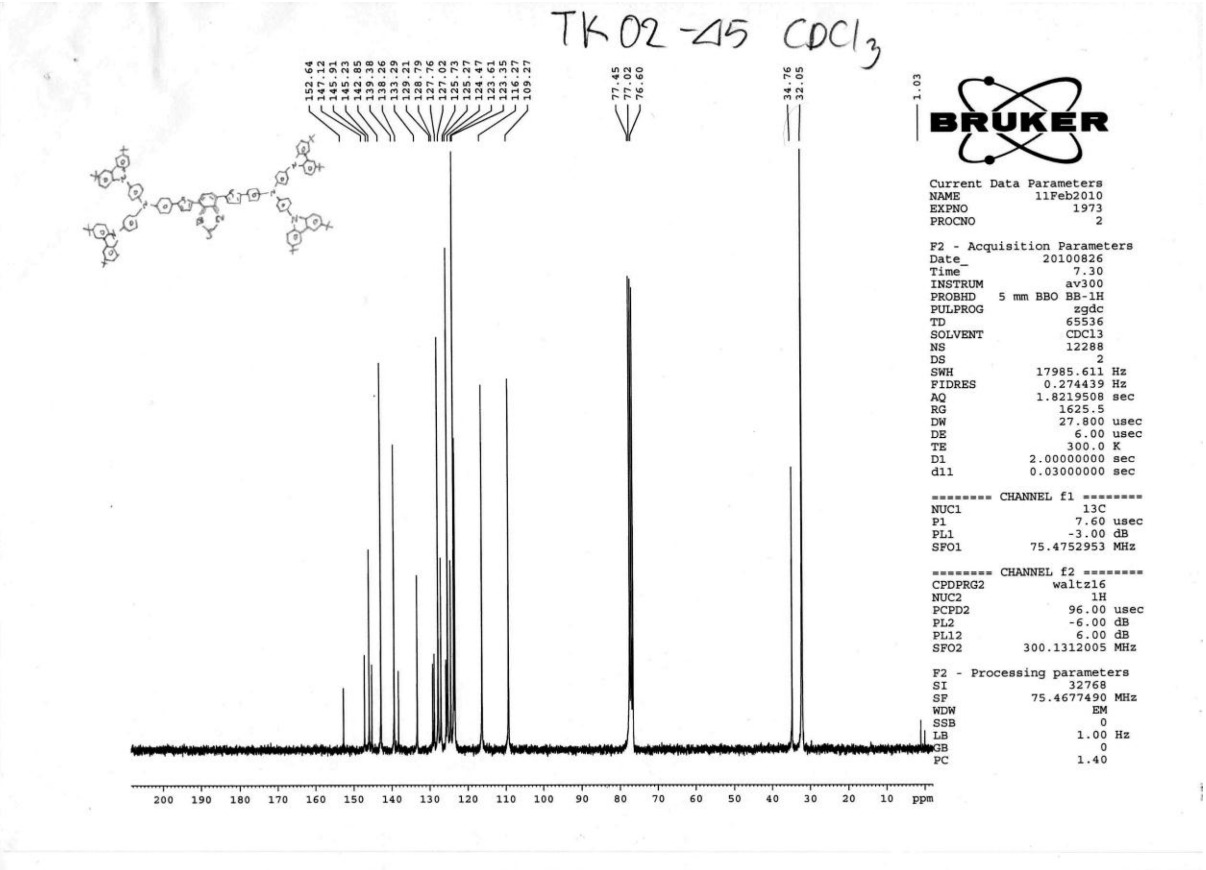
DS                      0
SWH              4496.403 Hz
FIDRES           0.137219 Hz
AQ              3.6438515 sec
RG                    128
DW                111.200 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  16.50 usec
PL1                 -6.00 dB
SFO1          300.1313506 MHz

F2 - Processing parameters
SI                  16384
SF            300.1300053 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```



```
Current Data Parameters
NAME            11Feb2010
EXPNO                1973
PROCNO                  2

F2 - Acquisition Parameters
Date_            20100826
Time                 7.30
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  65536
SOLVENT             CDCl3
NS                  12288
DS                      2
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                 1625.5
DW                 27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.60 usec
PL1                 -3.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               96.00 usec
PL2                 -6.00 dB
PL12                 6.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```