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Supplementary materials

I. Instrumentation and materials

Differential scanning calorimetry (DSC) measurements were performed using a DSC Q2000 calorimeter (TA Instruments) under N₂ environment. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 apparatus.

Cyclic voltammetry measurements were carried out on a μ -Autolab Type III potentiostat. Electrochemical experiments were carried out at room temperature using a three-electrode cell: platinum coil as counter electrode, a glassy carbon working electrode, and a silver wire as reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) was used as supporting electrolyte at a scan rate of 100 mVs⁻¹. For the measurements, silver reference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an internal standard.¹

Photoluminescence (PL) and UV spectra were recorded with the Edinburgh Instruments FLS980 and PerkinElmer Lambda 25 spectrometers, respectively. To separate the phosphorescence spectra, emission spectrum was recorded at 77 K with the delay time exceeding 50 ms. PL quantum yields of the films were estimated using FLS980 (Edinburgh Instruments Ltd.) equipped with integrating sphere under air condition. Photoluminescence decay curves were taken exploiting the PicoQuant LDH-D-C-375 laser (wavelength 374 nm) as the excitation source. Ionization potentials (I_p) of the films of the synthesized compounds were measured by electron photoemission spectrometry in air as reported earlier.

Photoelectron emission (PE) spectroscopy was used for the determination of ionization potentials (IP_{PE}) of vacuum-deposited organic layers. The PE setup contained deep UV deuterium light source ASBN-D130-CM, monochromator CM110 1/8m and electrometer 6517BKeithley. Under energy scan of the incident photons with increasing of photon energy, electrons were emitted (current on the counter electrode was detected) from the layer after reaching of photon energy higher than I_{EP} of tested compounds.

Time of flight (TOF) experiments. TOF samples with a structure glass/indium tin oxide (ITO)/organic layer /Al (100 nm) were fabricated by thermos-vacuum deposition equipment from Kurt J. Lesker inbuilt in MB EcoVap4G glove box. Thicknesses (d) of organic layers was in range 1–3.75 μm and an active area of samples was 6 mm^2 . The TOF measurements were provided in air at room temperature. Holes in the organic layer were generated by a laser pulse (Nd:YAG laser EKSPALA NL300) through electrode ITO to which a positive dc voltage was simultaneously applied. Forced by an electrical field (E), those holes were transported over the organic layer from ITO to Al. As a result of discharging of the holes at Al electrode, TOF transient photocurrents were recorded by a digital storage oscilloscope Tektronix TDS 3032C. A similar setup was used in charge extraction by the linearly increasing voltage (so-called dark-CELIV) measurements.^{2,3,4} Using the transit times (t_{tr}) from TOF transient photocurrents recorded at different voltages (V), calculation of hole mobility (μ) was provided by formula:

$$\mu = d^2 / (t_{tr} \times V).$$

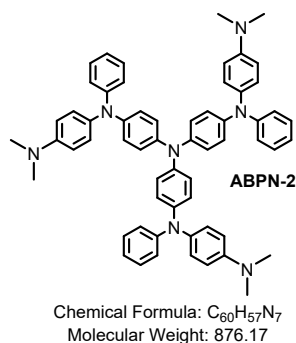
Using the times (t_{max}) taken at maximum extracted current from dark-CELIV transient photocurrents recorded at different duration times (t) and the same amplitude (V) of triangle pulses (at different rise speed $A=V/t$), μ as function of E was calculated using formula [17,18]:

$$\mu = \frac{2}{3} \times \frac{d^2}{A \cdot t_{max}^2 (1 + 0.36 \Delta j / j(0))},$$

where $j(0)$ is the capacitive displacement current and ΔJ is the conductivity current (extracted charges).

Device fabrication and characterization. OLEDs were fabricated via thermal vacuum deposition method using Kurt J. Lesker equipment inbuilt in a MB EcoVap4G glove box. The rate of deposition of organic layers was 1-2 Å/s. The deposition was made under the pressure of ca. $2 \cdot 10^{-6}$ mbar. The characterization of OLEDs was done by analysis of the data of simultaneous measurement of the current density, voltage and luminance of the EL of OLEDs done without passivation under air atmosphere. The measurements of OLEDs were managed using calibrated Keithley 2400C source meter, PH100-Si-HA-D0 photodiode, 11S-LINK Power and Energy Monitor and 6517B electrometer.

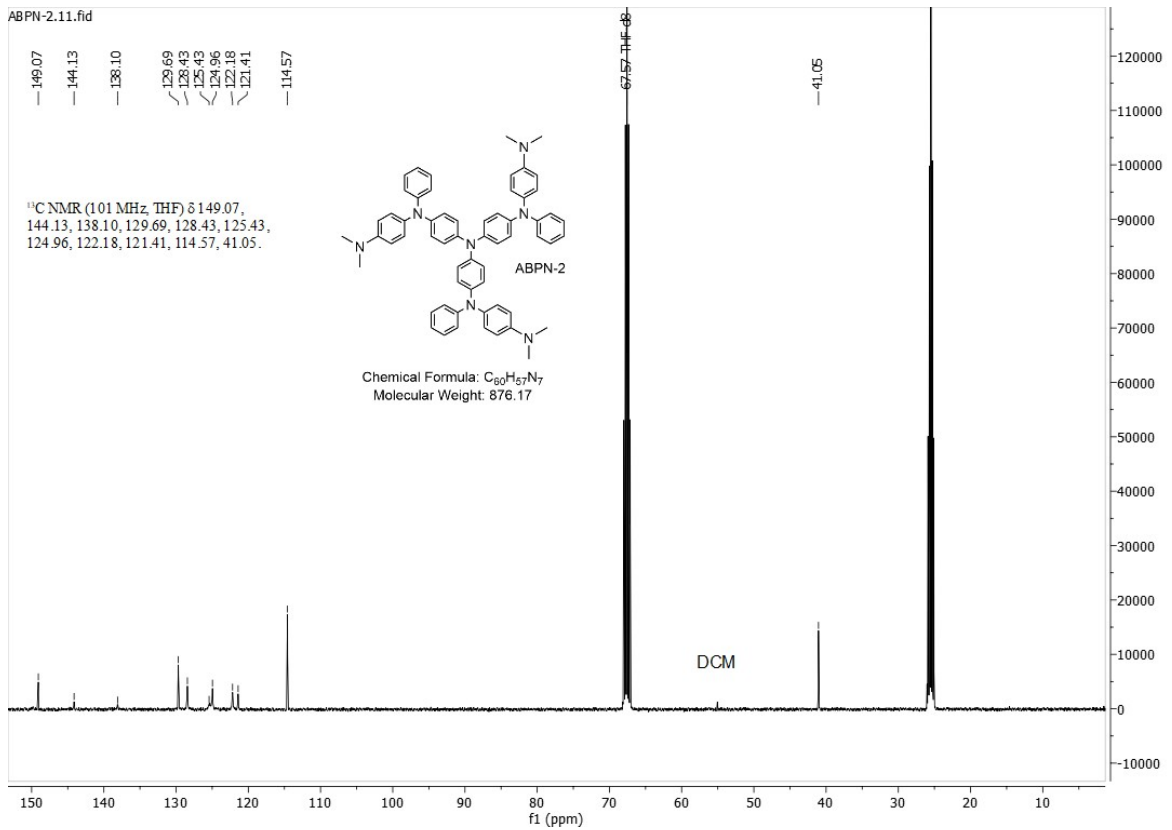
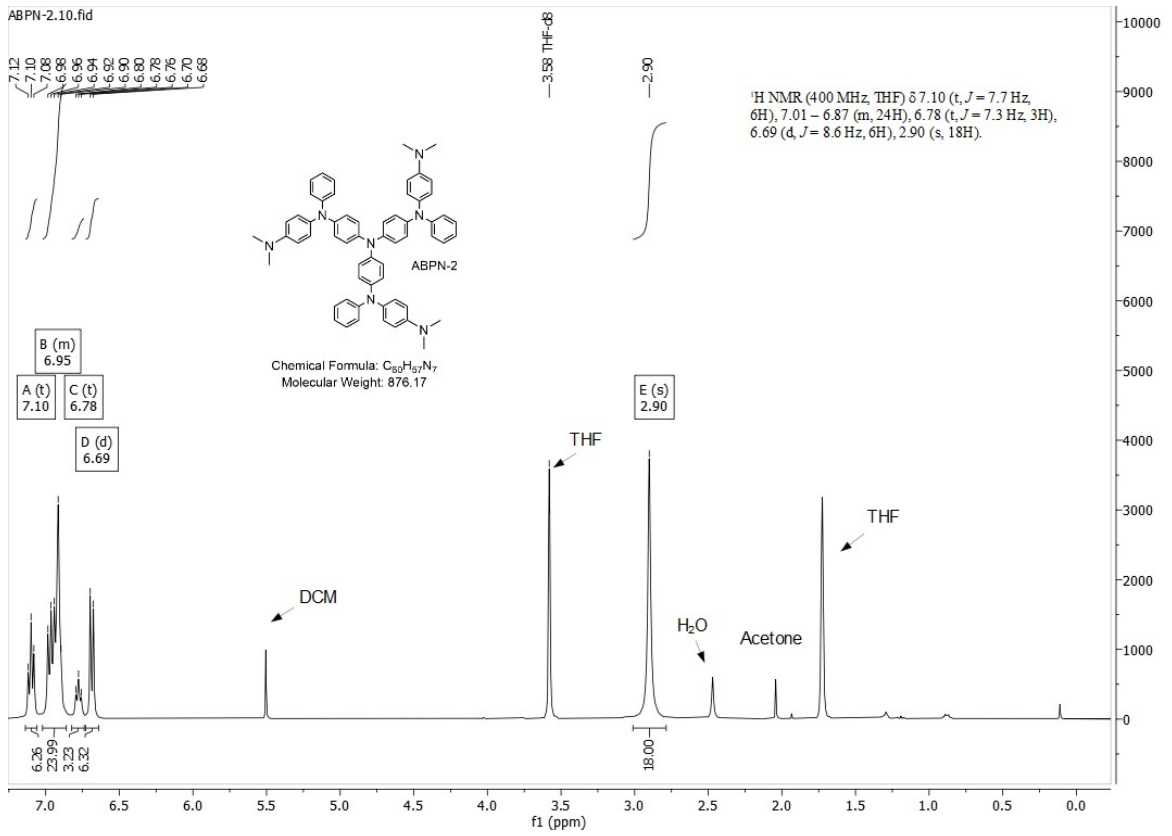
General synthesis procedure for Buchwald Hartwig cross coupling reaction of the synthesis of the target compounds (**ABM-2**, **ABE-2**, **ABMM-2**, **AB3M-2**, **ABN-2**, **ABPN-2**). A mixture of 1.0 equiv. of tris(4-bromophenyl)amine and 3.5 equiv. of diphenylamine derivative, 4.0 equiv. of sodium tert-butoxide, 0.15 equiv. of bis(dibenzylideneacetone)palladium(0) ($\text{Pd}(\text{dba})_2$) and 0.27 equiv. of 2-dicyclohexylphosphino-2',4',6'-triisopropyl-1,1'-biphenyl (XPhos) in dry toluene were refluxed for 12 hours under argon at 120 °C. Then the mixture was cooled, filtered and extracted using dichloromethane and brine. The solvent was removed under reduced pressure and the residue was purified using column chromatography technique with the selected eluent.

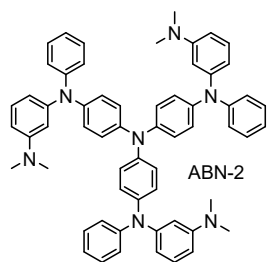


*N*¹-(4-(bis(4-((4-(dimethylamino)phenyl)(phenyl)amino)phenyl)amino)phenyl)-*N*⁴,*N*⁴-dimethyl-*N*¹-phenylbenzene-1,4-diamine (**ABPN-2**).

Compound **ABPN-2** ($C_{60}H_{57}N_7$) was synthesized following to the general procedure using tris(4-bromophenyl)amine (355 mg, 0.736 mmol), N^1,N^1 -dimethyl- N^4 -phenylbenzene-1,4-diamine (594 mg, 2.799 mmol), sodium *tert*-butoxide (283 mg, 2.946 mmol), $Pd_2(dba)_3$ (101 mg, 15 mol%), xphos (95 mg, 27 mol%) and 25 ml of dry toluene. The eluent used for column chromatography: hexane:ethylacetate:dichlormethane (10:1:1). The yellowish solid substance was obtained with the yield of 12 % (290 mg, FW = 876.17 g/mol). MS (ESI+) m/z = 876 $[M]^+$. 1H NMR (400 MHz, THF-*d*) δ 7.10 (t, J = 7.7 Hz, 6H), 7.01 – 6.87 (m, 24H), 6.78 (t, J = 7.3 Hz, 3H), 6.69 (d, J = 8.6 Hz, 6H), 2.90 (s, 18H). ^{13}C NMR (101 MHz, THF-*d*) δ 149.07, 144.13, 138.10, 129.69, 128.43, 125.43, 124.96, 122.18, 121.41, 114.57, 41.05.



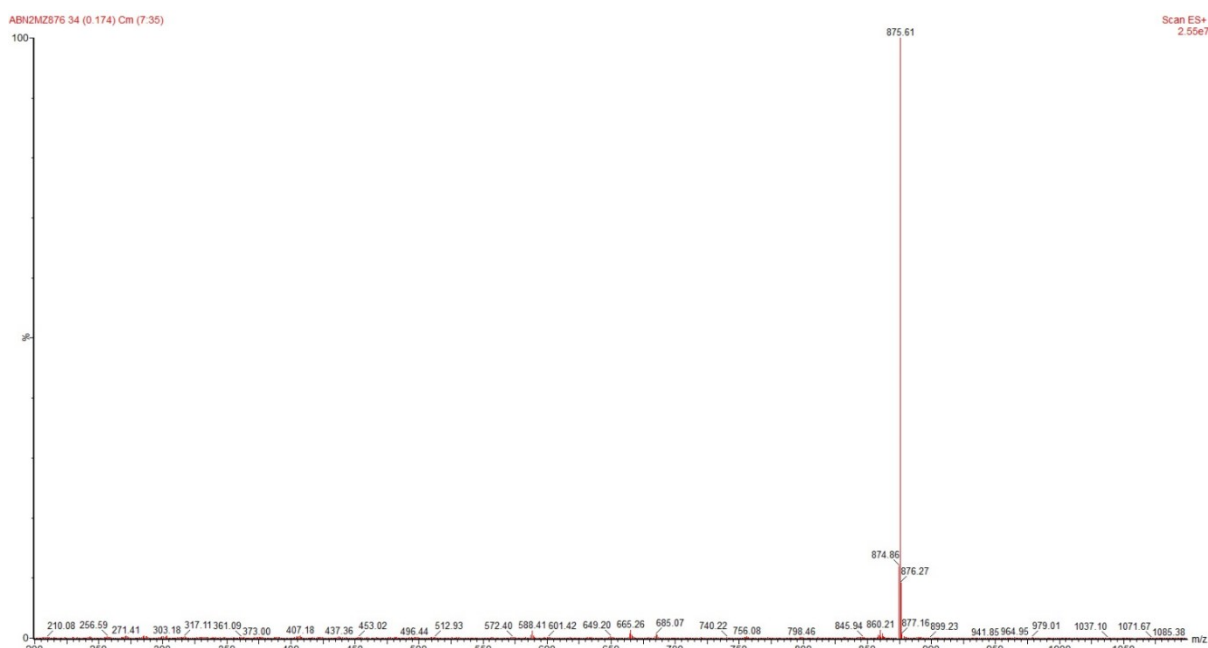


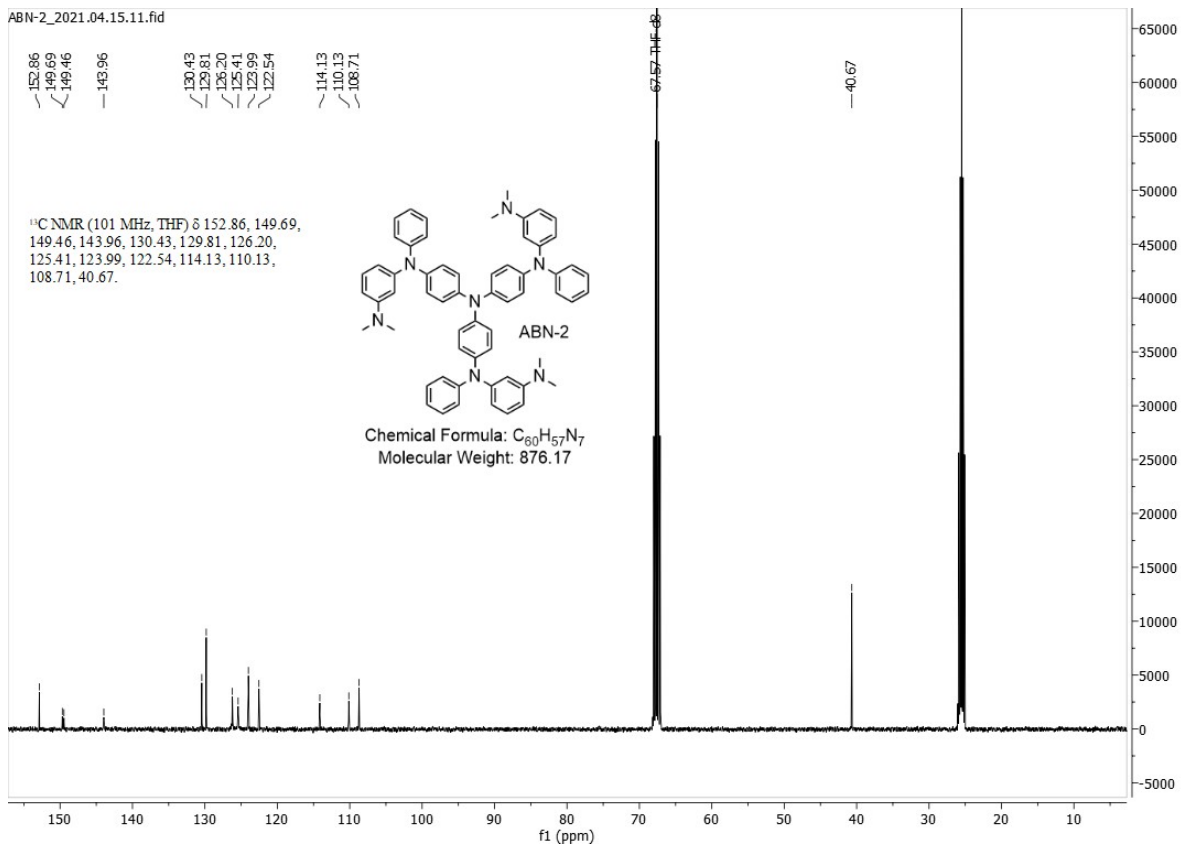
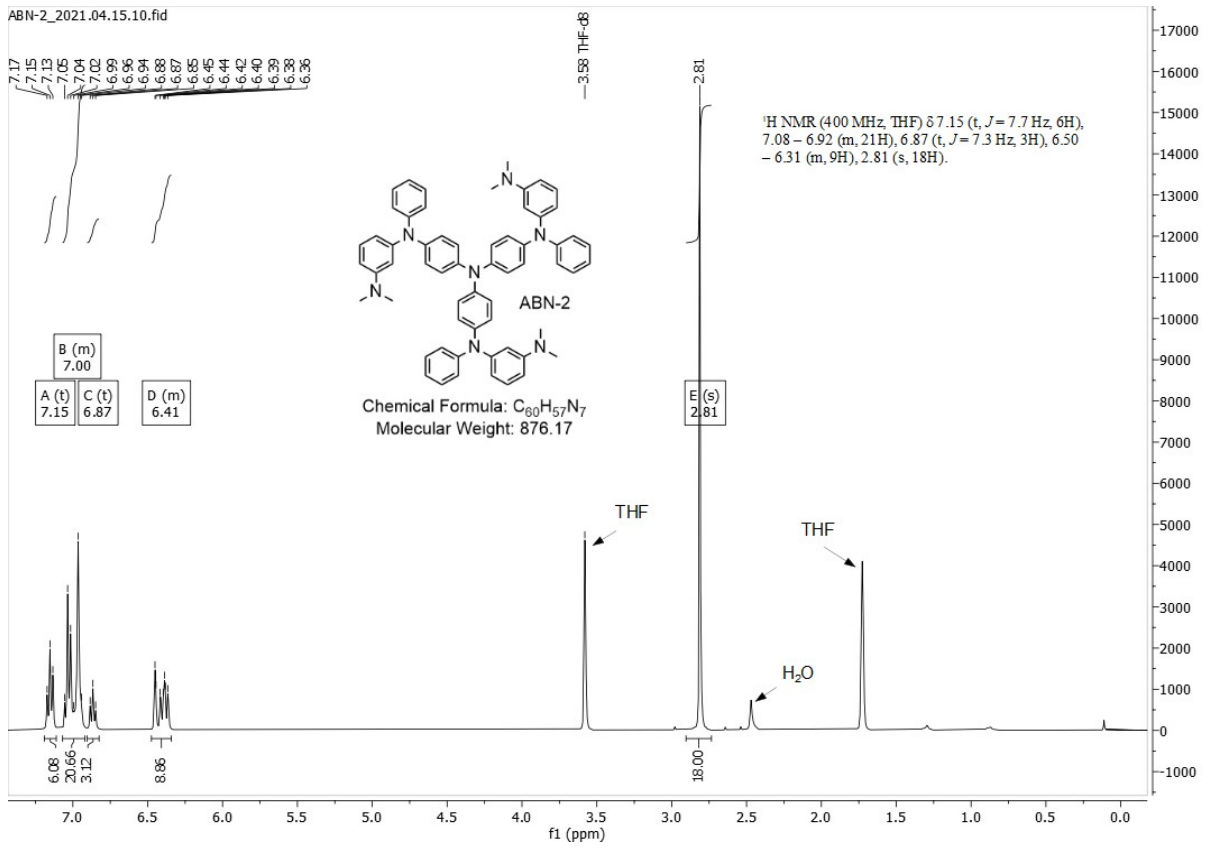


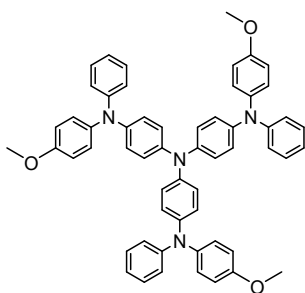
Chemical Formula: $C_{60}H_{57}N_7$
Molecular Weight: 876.17

*N*¹-4-(bis(4-((3-(dimethylamino)phenyl)(phenyl)amino)phenyl)amino)phenyl)-*N*³,*N*³-dimethyl-*N*¹-phenylbenzene-1,3-diamine (**ABN-2**).

Compound **ABN-2** ($C_{60}H_{57}N_7$) was synthesized following to the general procedure using tris(4-bromophenyl)amine (560 mg, 1.162 mmol), *N*¹,*N*¹-dimethyl-*N*³-phenylbenzene-1,3-diamine (913 mg, 4.299 mmol), sodium *tert*-butoxide (446 mg, 4.647 mmol), $Pd_2(dba)_3$ (159 mg, 15 mol%), *xphos* (150 mg, 27 mol%) and 25 ml of dry toluene. The eluent used for column chromatography: hexane:ethylacetate:dichlormethane (10:1:1). The yellowish solid substance was obtained with the yield of 11 % (415 mg, FW = 876.17 g/mol). MS (ESI+) m/z = 876 [M]⁺. ¹H NMR (400 MHz, THF-*d*) δ 7.15 (t, *J* = 7.7 Hz, 6H), 7.08 – 6.92 (m, 21H), 6.87 (t, *J* = 7.3 Hz, 3H), 6.50 – 6.31 (m, 9H), 2.81 (s, 18H). ¹³C NMR (101 MHz, THF-*d*) δ 152.86, 149.69, 149.46, 143.96, 130.43, 129.81, 126.20, 125.41, 123.99, 122.54, 114.13, 110.13, 108.71, 40.67.



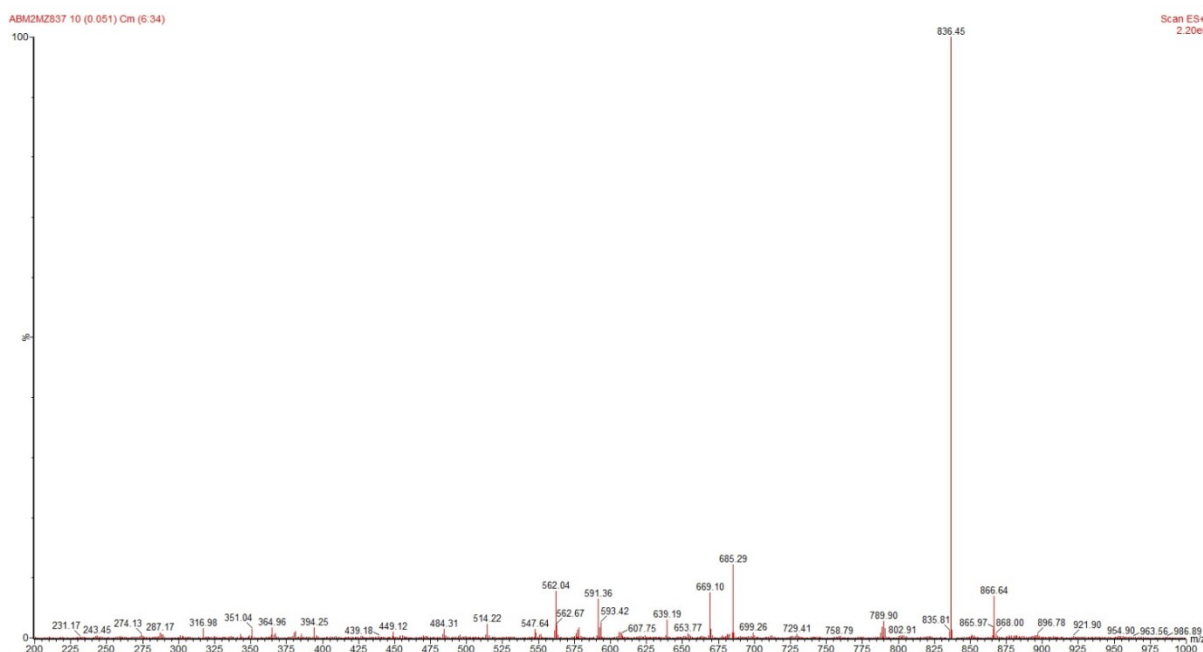


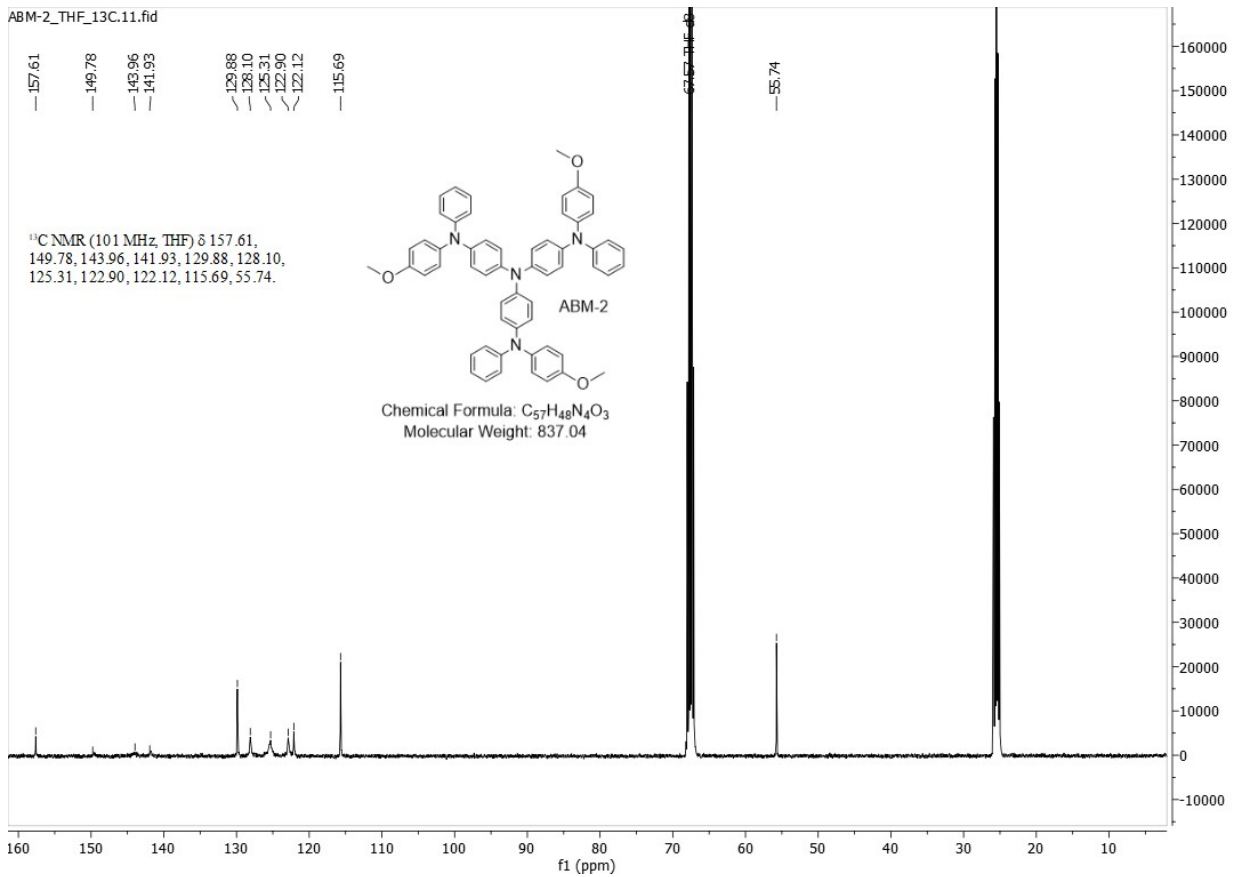
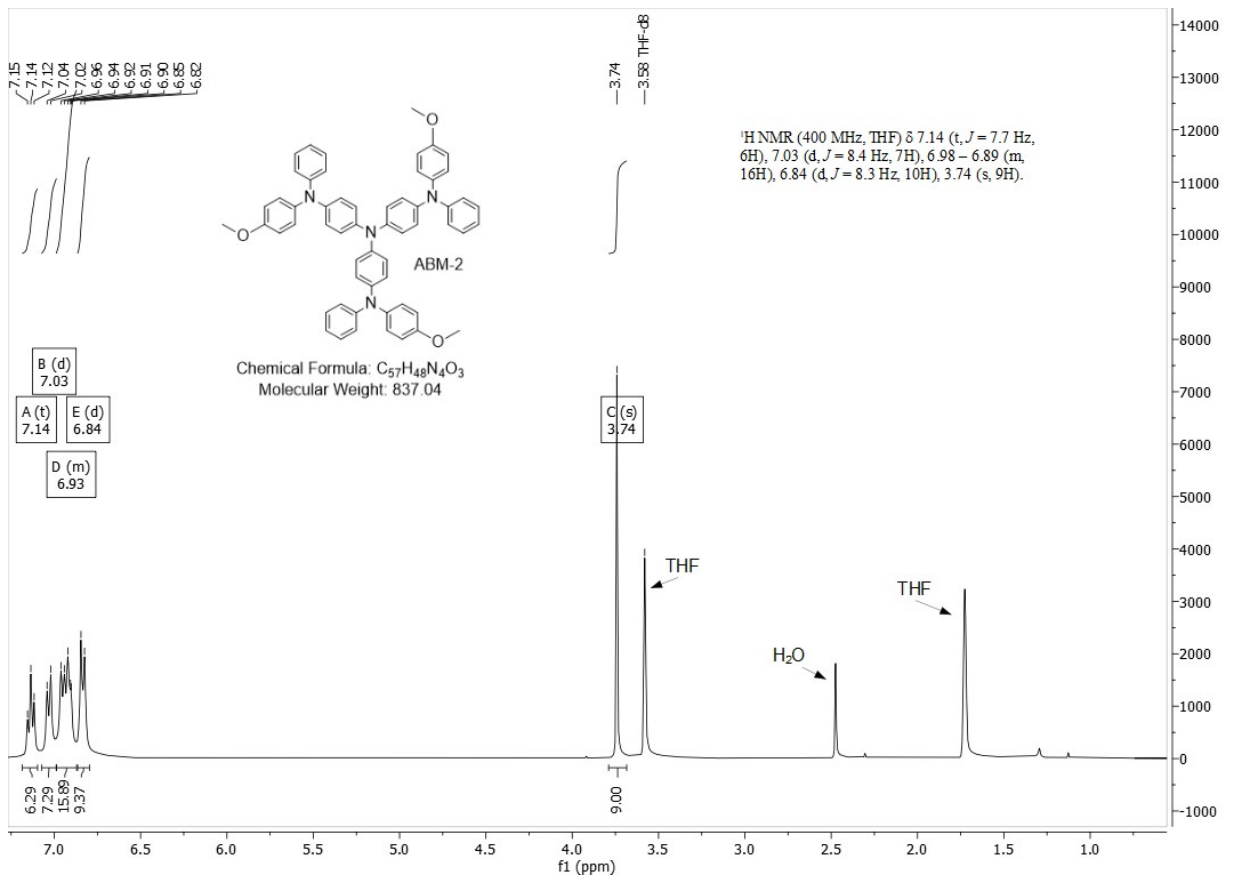


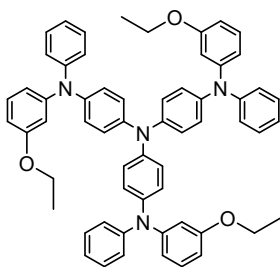
Chemical Formula: $C_{57}H_{48}N_4O_3$
Molecular Weight: 837.04

*N*¹-(4-methoxyphenyl)-*N*⁴,*N*⁴-bis(4-((4-methoxyphenyl)(phenyl)amino)phenyl)-*N*¹-phenylbenzene-1,4-diamine (**ABM-2**)

Compound **ABM-2** ($C_{57}H_{48}N_4O_3$) was synthesized following to the general procedure using tris(4-bromophenyl)amine (430 mg, 0.892 mmol), 4-methoxy-N-phenylaniline (640 mg, 3.212 mmol), sodium *tert*-butoxide (343 mg, 3.568 mmol), $Pd_2(dba)_3$ (122 mg, 15 mol%), xphos (115 mg, 27 mol%) and 25 ml of dry toluene. The eluent used for column chromatography: hexane:ethylacetate:dichlormethane (10:1:1). The yellow solid substance was obtained with the yield of 10 % (268 mg, FW = 837.04 g/mol). MS (ESI+) m/z = 837 [M]⁺. ¹H NMR (400 MHz, THF-*d*) δ 7.14 (t, J = 7.7 Hz, 6H), 7.03 (d, J = 8.4 Hz, 7H), 6.98 – 6.89 (m, 16H), 6.84 (d, J = 8.3 Hz, 10H), 3.74 (s, 9H). ¹³C NMR (101 MHz, THF-*d*) δ 157.61, 149.78, 143.96, 141.93, 129.88, 128.10, 125.31, 122.90, 122.12, 115.69, 55.74.



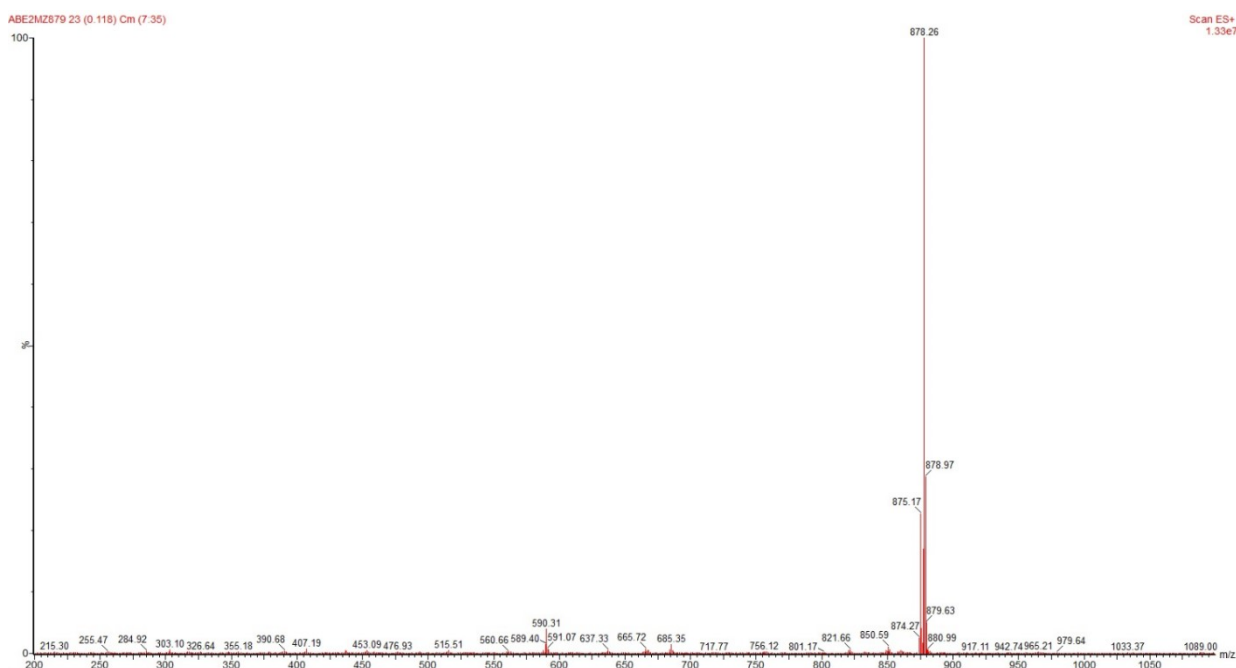


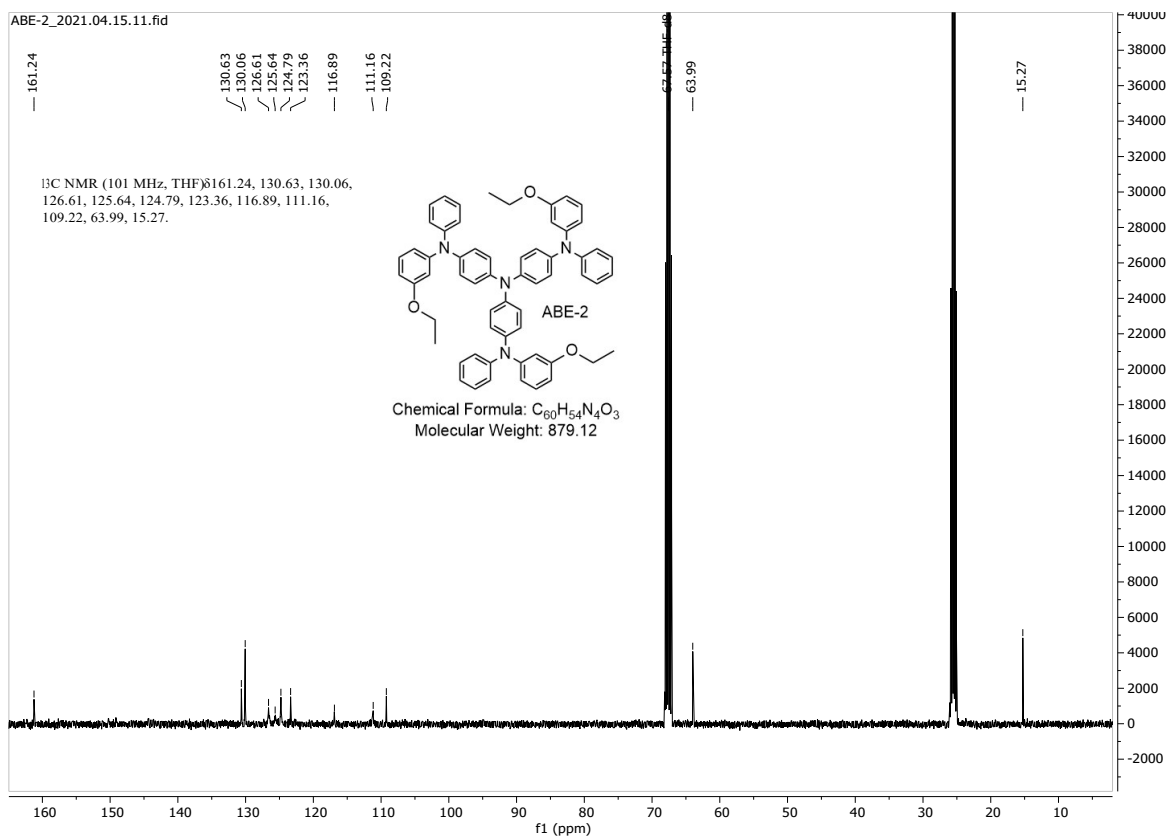
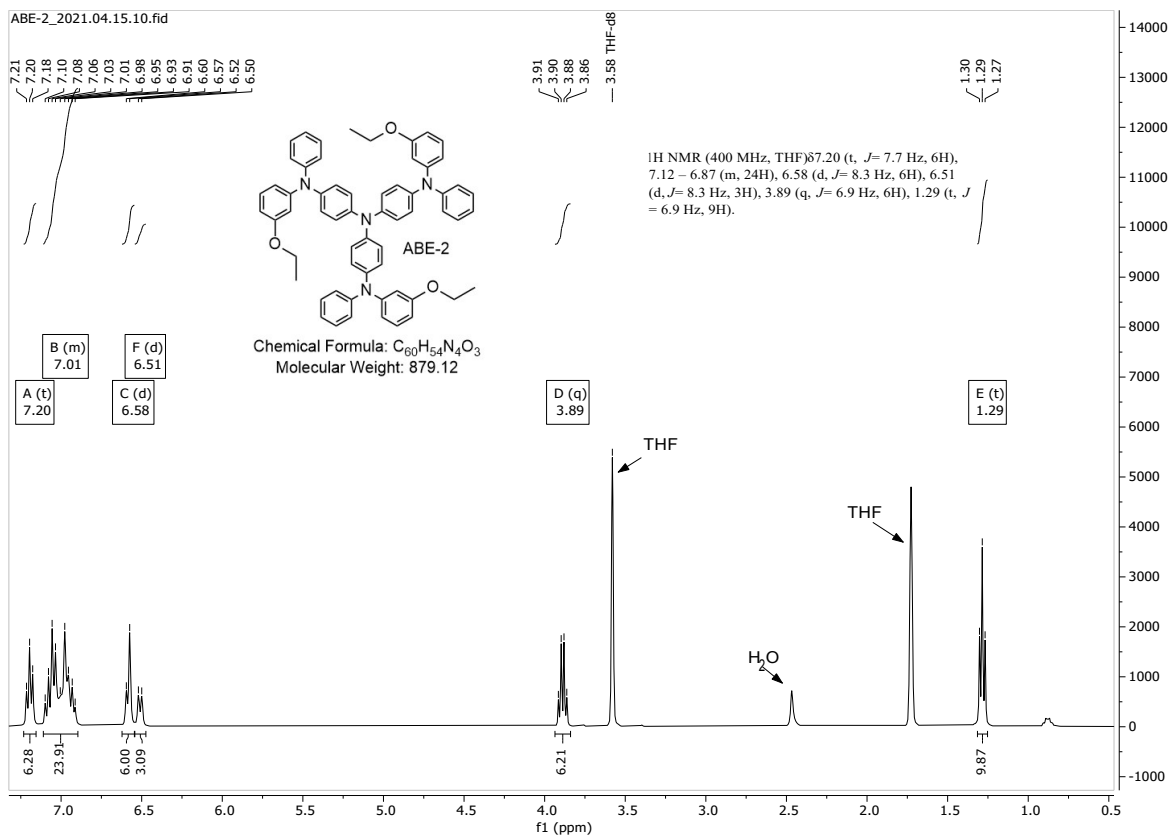


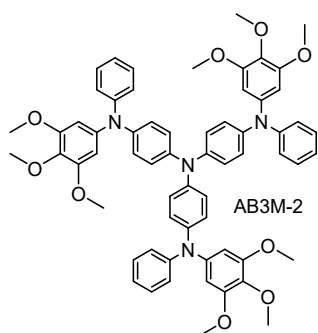
Chemical Formula: $C_{60}H_{54}N_4O_3$
Molecular Weight: 879.12

*N*¹-(3-ethoxyphenyl)-*N*⁴,*N*⁴-bis(4-((3-ethoxyphenyl)(phenyl)amino)phenyl)-*N*¹-phenylbenzene-1,4-diamine (**ABE-2**)

Compound **ABE-2** ($C_{60}H_{54}N_4O_3$) was synthesized following to the general procedure using tris(4-bromophenyl)amine (420 mg, 0.871 mmol), 3-ethoxy-N-phenylaniline (632 mg, 2.963 mmol), sodium *tert*-butoxide (335 mg, 3.485 mmol), $Pd_2(dba)_3$ (120 mg, 15 mol%), xphos (112 mg, 27 mol%) and 25 ml of dry toluene. The eluent used for column chromatography: hexane:ethylacetate:dichloromethane (10:1:1). The yellow solid substance was obtained with the yield of 18 % (470 mg, FW = 837.04 g/mol). MS (ESI+) m/z = 879 $[M]^+$. ¹H NMR (400 MHz, THF-*d*) δ 7.20 (t, *J* = 7.7 Hz, 6H), 7.12 – 6.87 (m, 24H), 6.58 (d, *J* = 8.3 Hz, 6H), 6.51 (d, *J* = 8.3 Hz, 3H), 3.89 (q, *J* = 6.9 Hz, 6H), 1.29 (t, *J* = 6.9 Hz, 9H). ¹³C NMR (101 MHz, THF-*d*) δ 161.24, 130.63, 130.06, 126.61, 125.64, 124.79, 123.36, 116.89, 111.16, 109.22, 63.99, 15.27.



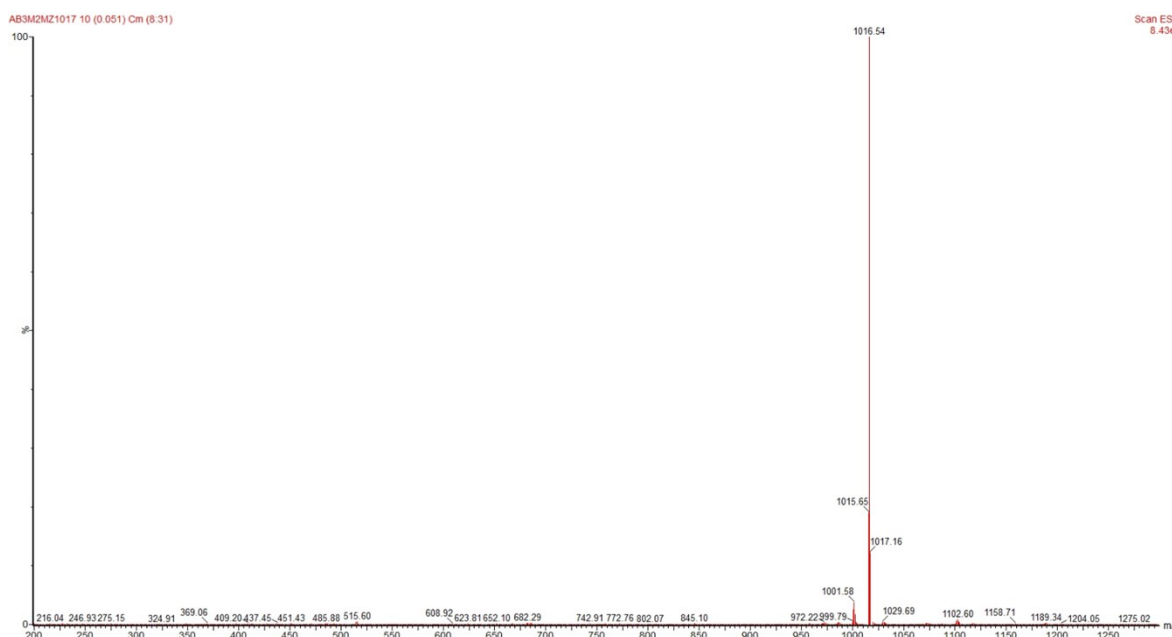


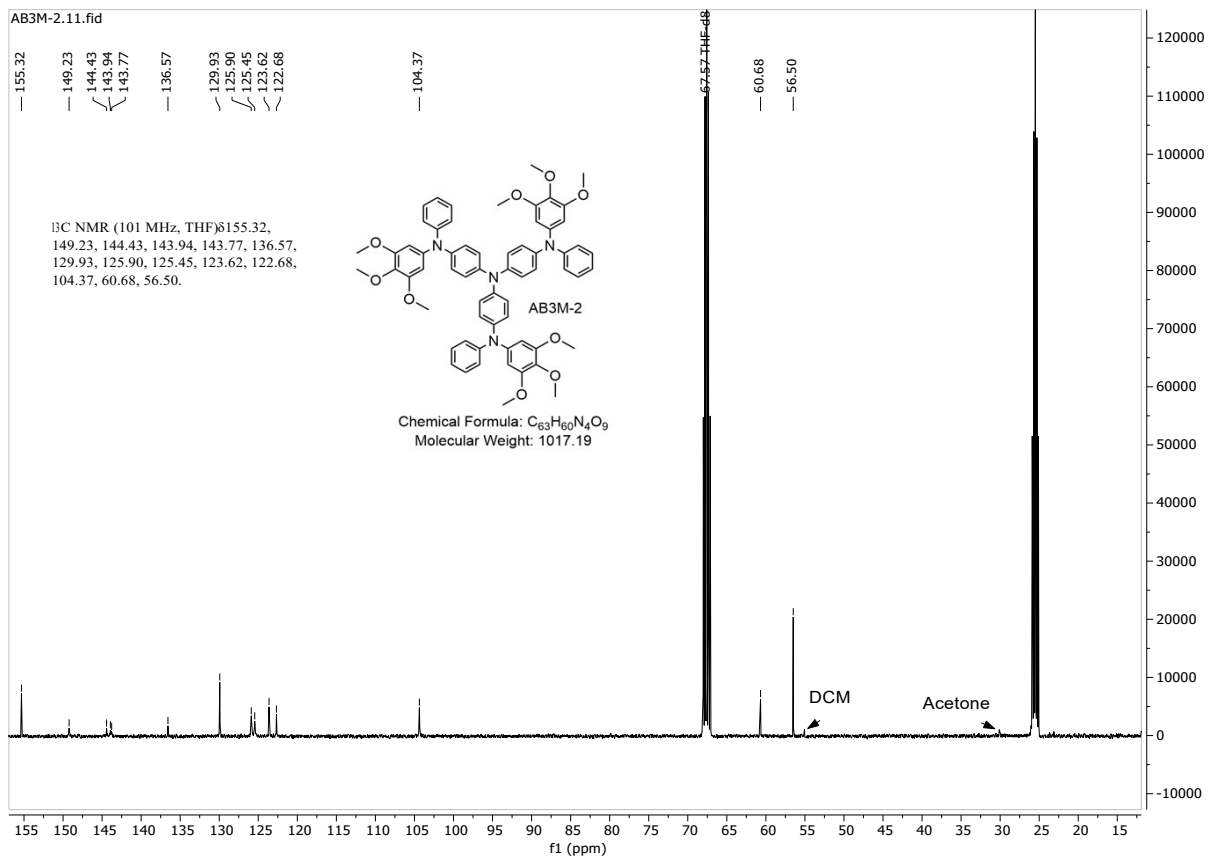
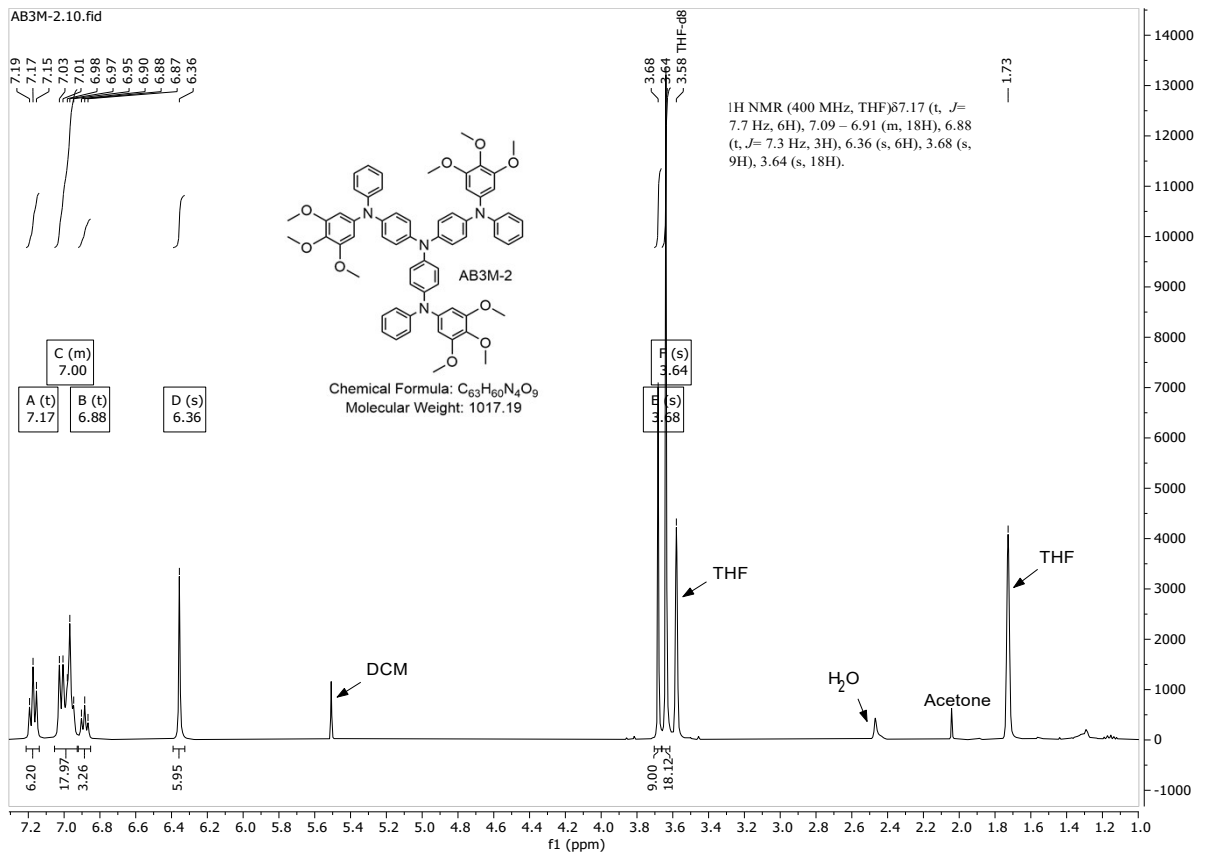


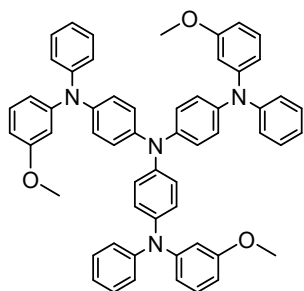
Chemical Formula: C₆₃H₆₀N₄O₉
Molecular Weight: 1017.19

*N*¹-phenyl-*N*⁴,*N*⁴-bis(4-(phenyl(3,4,5-trimethoxyphenyl)amino)phenyl)-*N*¹-(3,4,5-trimethoxyphenyl) benzene-1,4-diamine (**ABM3-2**)

Compound **AB3M-2** (C₆₃H₆₀N₄O₉) was synthesized following to the general procedure using tris(4-bromophenyl)amine (590 mg, 1.224 mmol), 3,4,5-trimethoxy-N-phenylaniline (1111 mg, 4.284 mmol), sodium *tert*-butoxide (470 mg, 4.896 mmol), Pd₂(dba)₃ (168 mg, 15 mol%), xphos (158 mg, 27 mol%) and 30 ml of dry toluene. The eluent used for column chromatography was hexane:ethylacetate:dichlormethane (10:1:1). The yellow solid substance was obtained with the yield of 18.5 % (700 mg, FW = 837.04 g/mol). MS (ESI+) *m/z*= 1017 [M]⁺. ¹H NMR (400 MHz, THF-*d*) δ 7.17 (t, J = 7.7 Hz, 6H), 7.09 – 6.91 (m, 18H), 6.88 (t, J = 7.3 Hz, 3H), 6.36 (s, 6H), 3.68 (s, 9H), 3.64 (s, 18H). ¹³C NMR (101 MHz, THF) δ 155.32, 149.23, 144.43, 143.94, 143.77, 136.57, 129.93, 125.90, 125.45, 123.62, 122.68, 104.37, 60.68, 56.50.





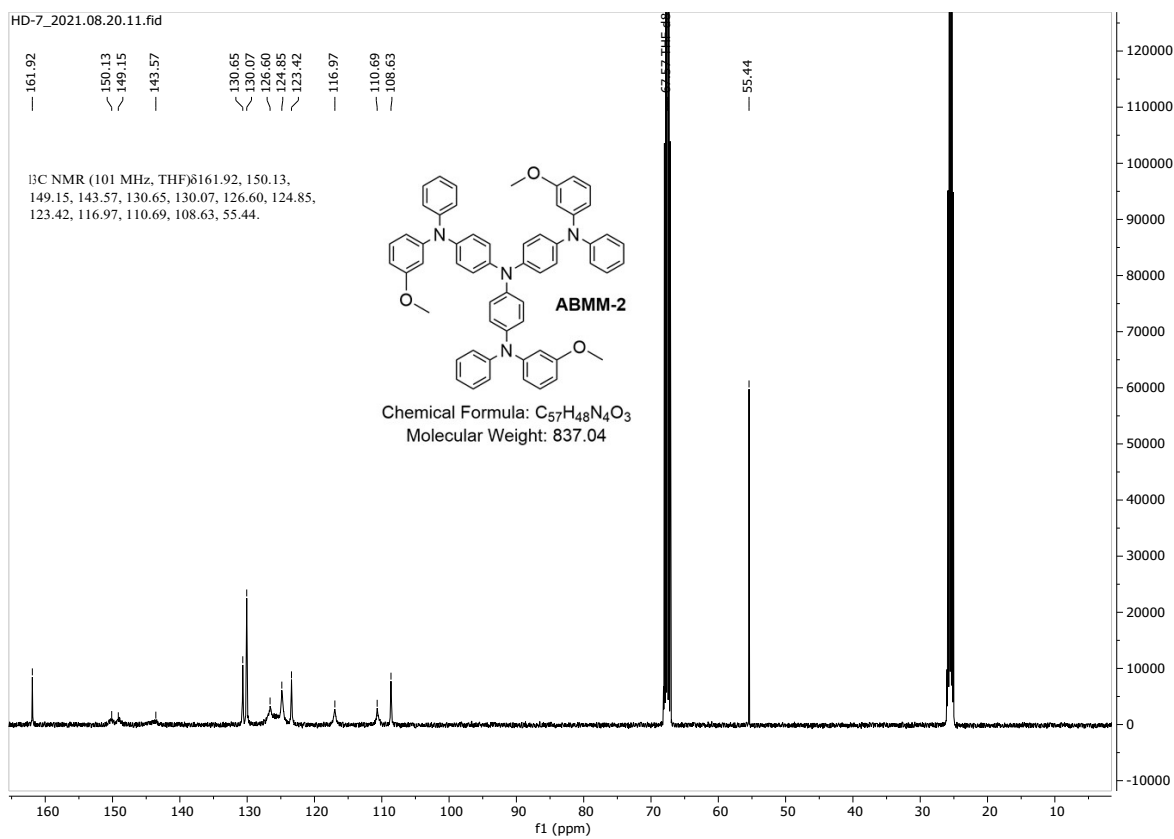
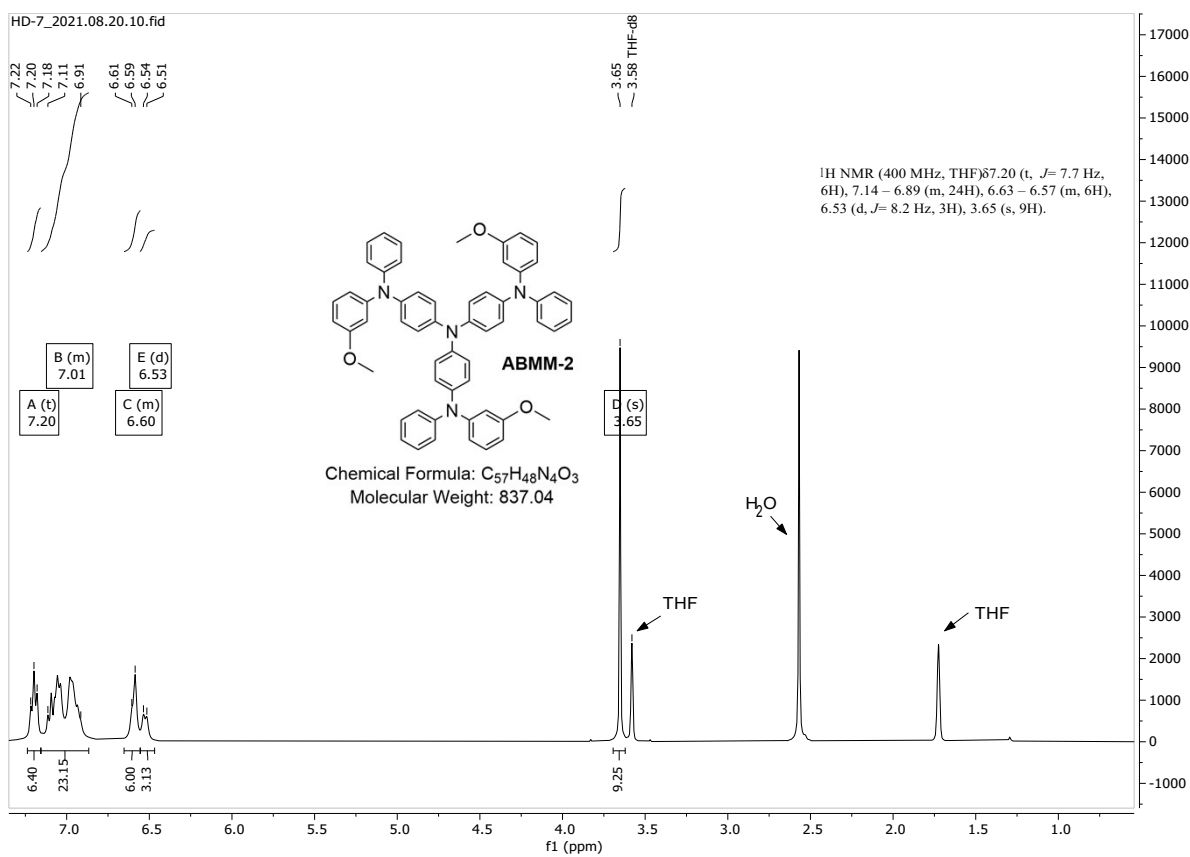


Chemical Formula: $C_{57}H_{48}N_4O_3$

Molecular Weight: 837.04

*N*¹-(3-methoxyphenyl)-*N*⁴,*N*⁴-bis(4-((3-methoxyphenyl)(phenyl)amino)phenyl)-*N*¹-phenylbenzene-1,4-diamine (**ABMM-2**)

Compound **ABMM-2** ($C_{57}H_{48}N_4O_3$) was synthesized following to the general procedure using tris(4-bromophenyl)amine (600 mg, 1.245 mmol), 3-methoxy-N-phenylaniline (893 mg, 4.481 mmol), sodium *tert*-butoxide (478 mg, 4.979 mmol), $Pd_2(dba)_3$ (171 mg, 15 mol%), xphos (160 mg, 27 mol%) and 25 ml of dry toluene. The eluent used for column chromatography was hexane:ethylacetate:dichlormethane (10:1:1). The yellow solid substance was obtained with the yield of 28 % (1050 mg, FW = 837.04 g/mol). MS (ESI+) m/z = 837 [M]⁺. ¹H NMR (400 MHz, THF) δ 7.20 (t, J = 7.7 Hz, 6H), 7.14 – 6.89 (m, 24H), 6.63 – 6.57 (m, 6H), 6.53 (d, J = 8.2 Hz, 3H), 3.65 (s, 9H). ¹³C NMR (101 MHz, THF-*d*) δ 161.92, 150.13, 149.15, 143.57, 130.65, 130.07, 126.60, 124.85, 123.42, 116.97, 110.69, 108.63, 55.44.



II. Thermal, optical, photophysical, optoelectrical properties.

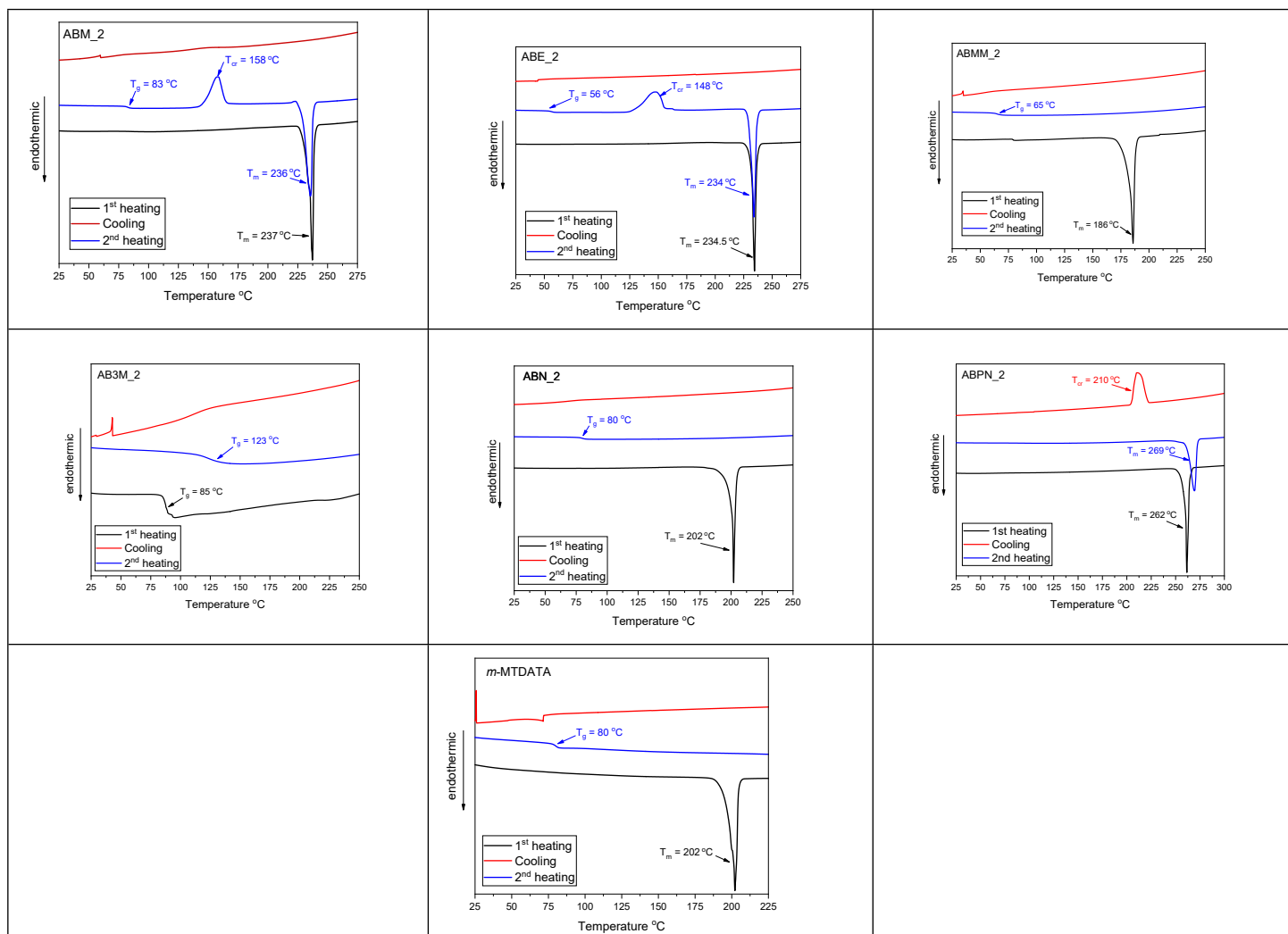


Figure S1. DSC thermograms of ABM-2, ABE-2, ABMM-2, AB3M-2, ABN-2, ABPN-2 and *m*-MTDATA.

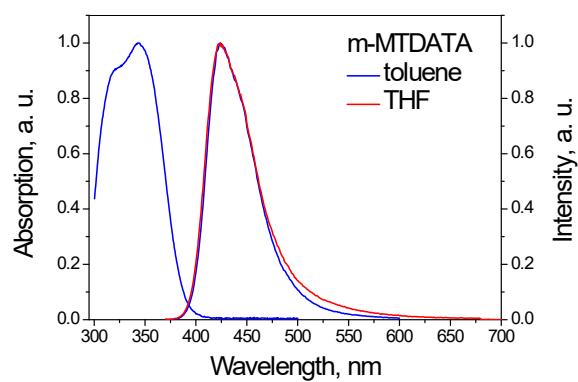


Figure S2. Absorption and PL spectra of dilute toluene and THF solutions of *m*-MTDATA recorded at room temperature.

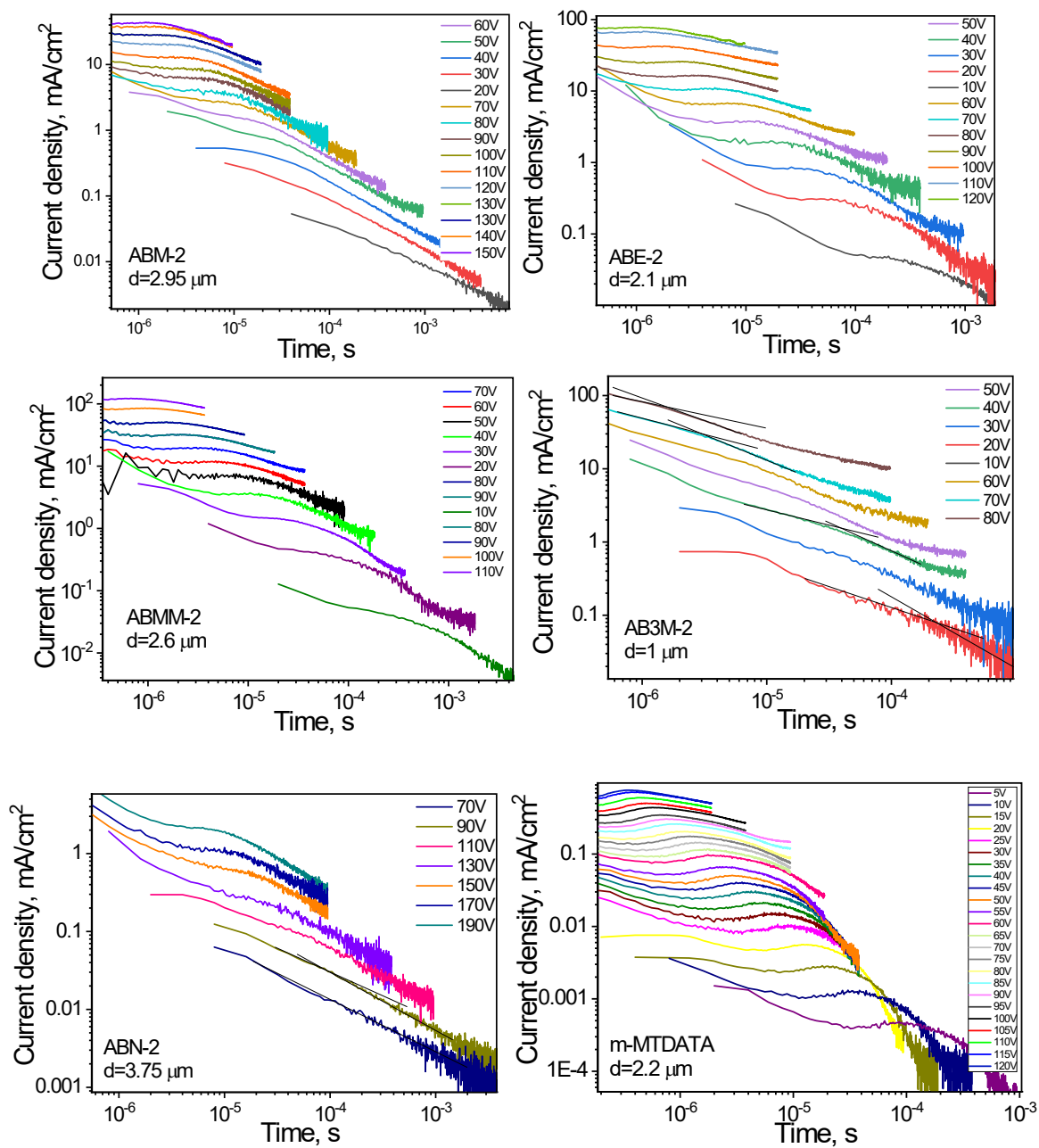


Figure S3. TOF current transients at different voltages (electric fields) for the studied organic layers.

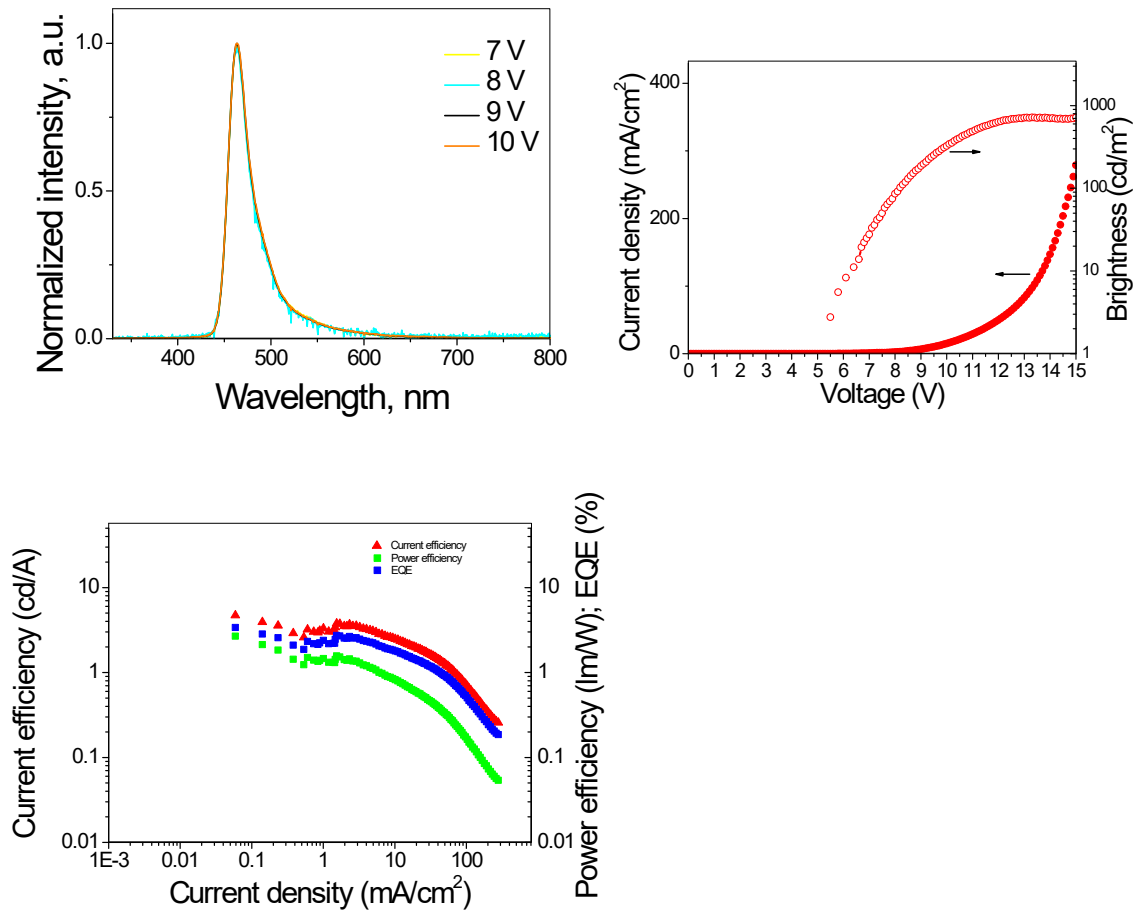
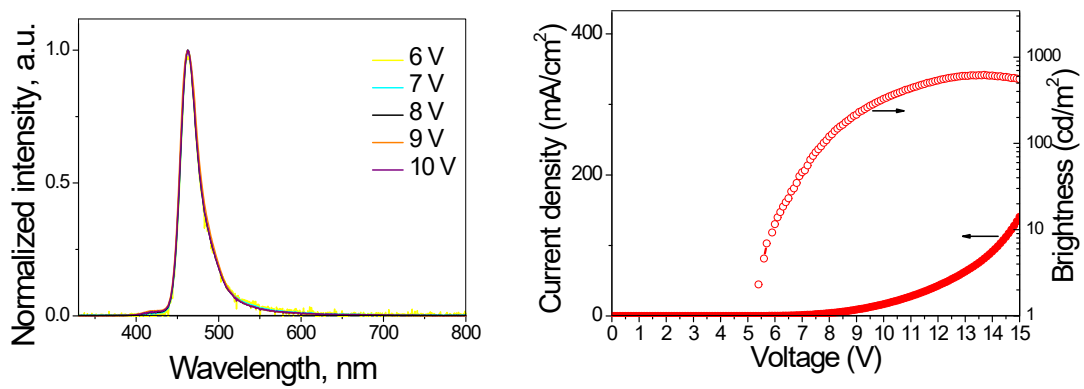


Figure S4. A OLED. EL spectra, current density-brightness-voltage, current efficiency-power efficiency-EQE-current density correlation



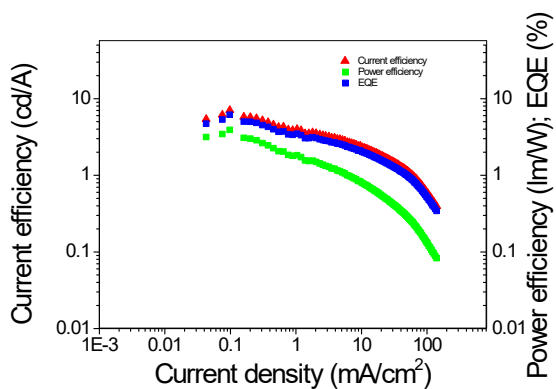


Figure S5. B OLED. EL spectra, current density-brightness-voltage, current efficiency-power efficiency-EQE-current density correlation

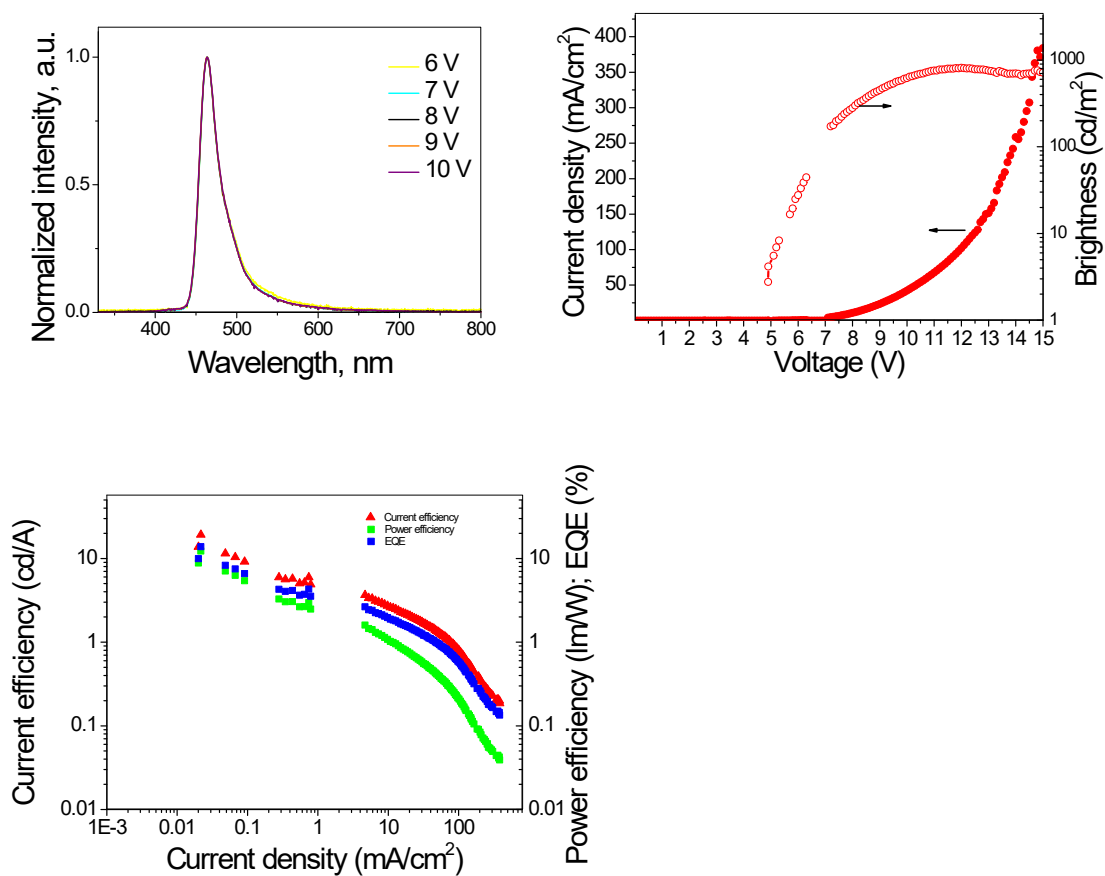


Figure S6. C OLED. EL spectra, current density-brightness-voltage, current efficiency-power efficiency-EQE-current density correlation.

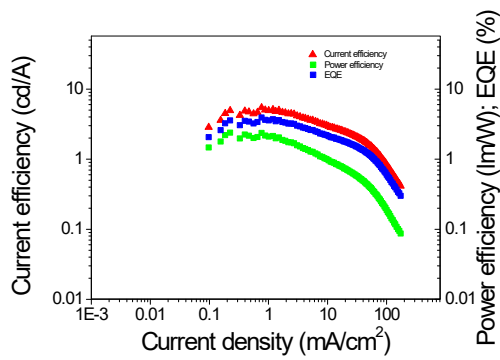
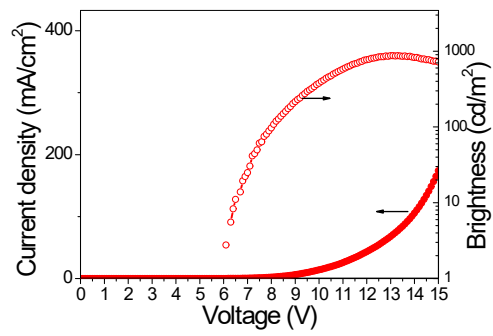
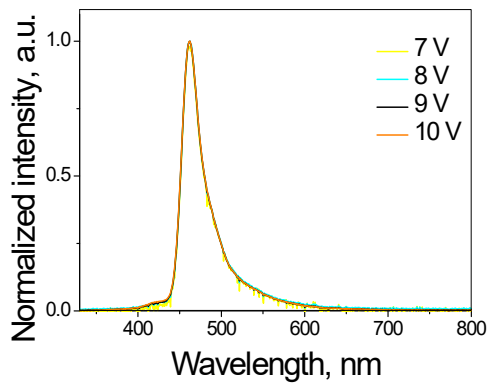
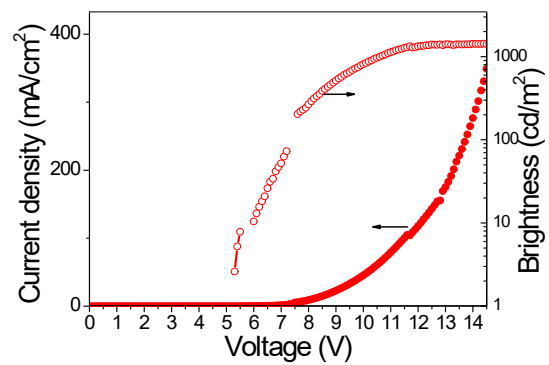
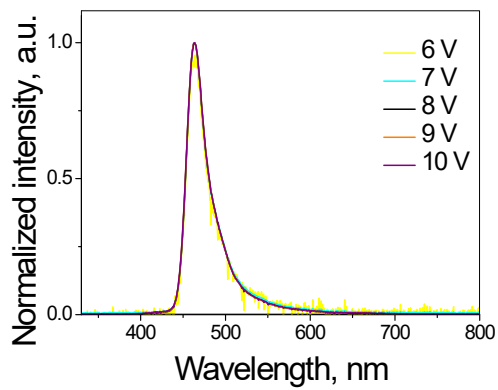


Figure S7. D OLED. EL spectra, current density-brightness-voltage, current efficiency-power efficiency-EQE-current density correlation



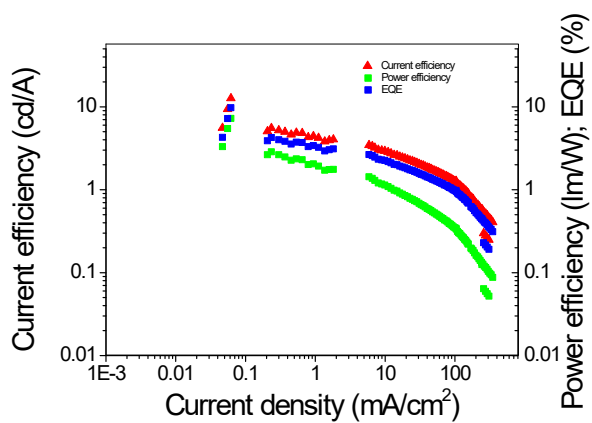


Figure S8. E OLED. EL spectra, current density-brightness-voltage, current efficiency-power efficiency-EQE-current density correlation

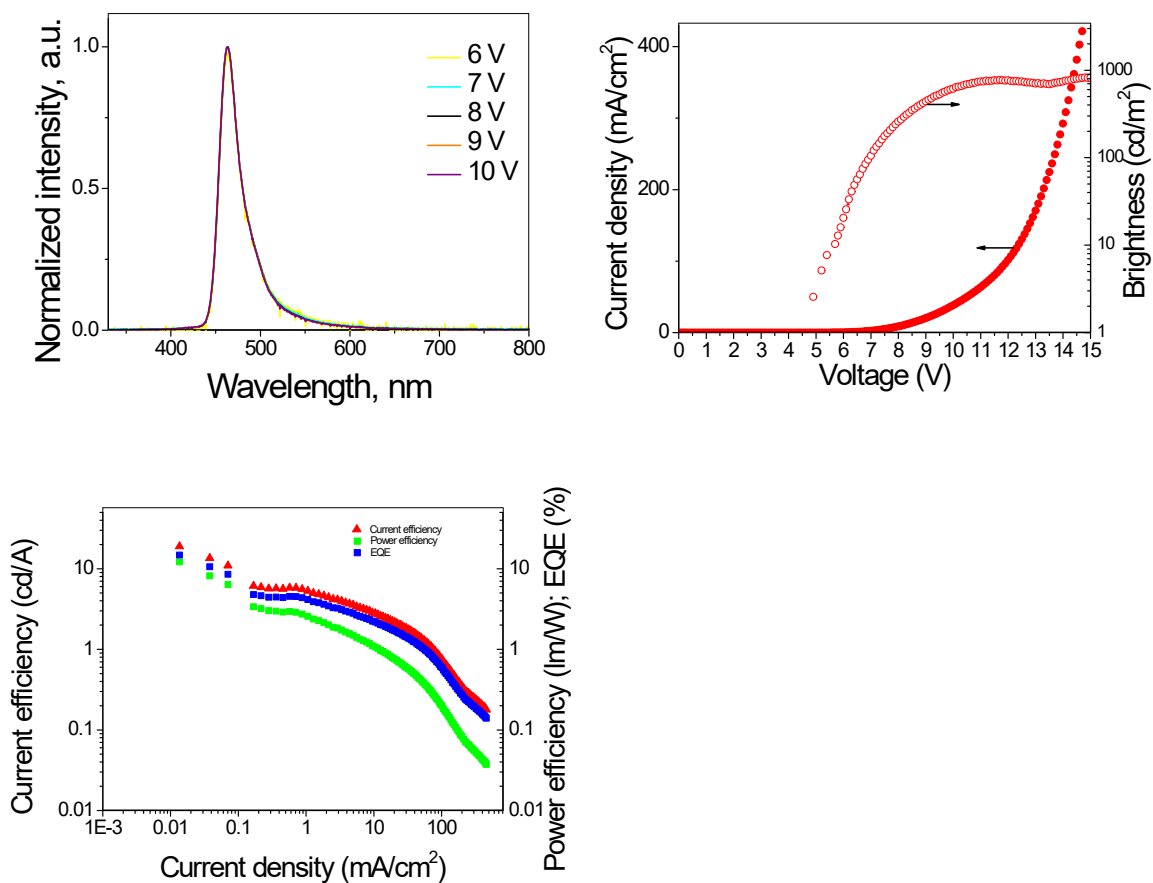


Figure S9. F OLED. EL spectra, current density-brightness-voltage, current efficiency-power efficiency-EQE-current density correlation.

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- 1 G. Gritzner and J. Kůta, *Electrochim. Acta*, 1984, **29**, 869–873.
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