SUPPORTING INFORMATION

Acridinone/Amine (Carbazole)-Based Bipolar Molecules: Efficient Hosts for Fluorescent and Phosphorescent Emitters

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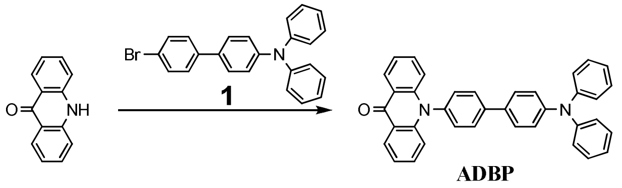
1. Synthesis

General. All reactions were carried out under nitrogen atmosphere and anhydrous conditions. Anhydrous solvents were purchased from Sigma-Aldrich Chemical Co. and were used as received. All reagents including catalysts and ligands were purchased from Sigma-Aldrich Chemical Co. and were used as received. Column chromatographic separations were performed using 60-230 mesh silica gel. NMR spectra were recorded on a Varian 300 spectrometer. The spectra were taken in $CDCl_3$ with TMS (0 ppm) as a reference standard for proton chemical shifts and $CDCl_3$ (77 ppm) as a reference standard for carbon-13 chemical shifts. 4-bromo-4'-(diphenylamino)biphenyl (**1**)[1] and 4-bromo-4'-(9-carbazolyl)biphenyl (**2**)[2] were prepared according literature procedures.



*Preparation of 10-(4'-(diphenylamino)biphenyl-4-yl)acridin-9(10H)-one (**ADBP**) : General procedure*: To an 100 mL dry, three-necked round flask were charged 4-bromo-4'-(diphenylamino)biphenyl (**1**, 2.0 g, 5 mmol), 9(10H)-acridone (1.17 g, 6 mmol), K_2CO_3 (1.0 g, 7.5 mmol), CuI (0.1g), 2,2,6,6-tetramethyl-3,5-heptanedione (0.2g), and anhydrous DMF (30 mL). The mixture was degassed and refluxed under nitrogen atmosphere for 24 h. After cooling to room temperature, the precipitates from the reaction mixture were collected by filtration, washed with 3 N HCl, water and methanol, and dried in air. The light yellow solid was dissolved in CH_2Cl_2 and purified by column chromatography on silica gel with CH_2Cl_2-EtOAc (40:1 v/v) as eluting solvents. The major fraction was collected and the removal of the solvents afforded 2.1 g of ADBP as a white solid. Yield: 82%. M.p.: > 250 °C. The material was further purified by sublimation for device fabrications. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.56-7.49 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.34-7.25 (m, 6H), 7.24-7.14 (m, 6H), 7.08 (t, J = 7.5 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 148.3, 147.7, 143.4, 142.3, 137.6, 133.5, 133.3, 130.6, 129.6, 129.3,

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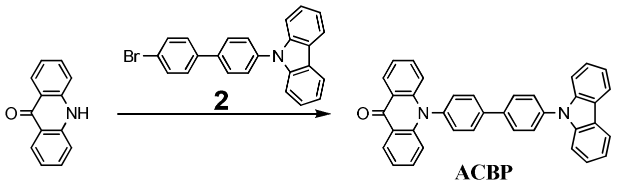
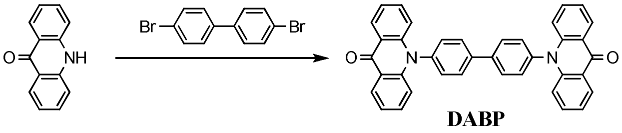
(1) Li, Z. H.; Wong, M. S.; Tao, Y.; D'Iorio, M. *J. Org. Chem.* **2004**, *69*, 921.
(2) Korene, B. E.; Loy, D. E.; Thompson, M. E. Chem. Mater. 1998, 10, 2235.

128.1, 127.6, 125.0, 123.7, 123.6, 122.1, 121.8, 117.2. Anal. Calcd for $C_{37}H_{26}N_2O$: C, 86.35; H, 5.09; N, 5.44. Found: C, 86.53; H, 5.15; N, 5.32.



*10-(4'-(9H-carbazol-9-yl)biphenyl-4-yl)acridin-9(10H)-one (**ACBP**)*: This compound was synthesized by cross coupling of 4-bromo-4'-(9-carbazolyl)biphenyl (**2**) with 9(10*H*)-acridinone according to the general procedure as a white solid. Yield: 82%. M.p.: > 250 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 7.8, 1.8 Hz, 2H), 8.19 (d, *J* = 7.8 Hz, 2H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.60-7.42 (m, 8H), 7.36-7.30 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 143.4, 141.9, 141.0, 138.9, 138.6, 138.0, 133.6, 130.9, 130.0, 128.9, 127.8, 127.7, 126.3, 123.8, 122.1, 121.9, 120.7, 120.4, 117.1, 110.0. Anal. Calcd for $C_{37}H_{24}N_2O$: C, 86.69; H, 4.72; N, 5.46. Found: C, 86.56; H, 4.74; N, 5.35.



*10,10'-(biphenyl-4,4'-diyl)diacridin-9(10H)-one (**DABP**):* This compound was synthesized cross coupling of 4, 4'-bromobiphenyl with 9(10H)-acridinone according to the general procedure as a white solid. Yield: 85%. M.p.: > 250 °C. This compound has very poor solubility in all organic solvents that have been tested including dichloromethane and chloroform, therefore its ^{13}C NMR spectrum has a very low signal/noise ratio. ^1H NMR (300 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 8.1, 1.2 Hz, 4H), 8.07 (d, *J* = 8.4 Hz, 4H), 7.60-7.52 (m, 8H), 7.33 (t, *J* = 7.5 Hz, 4H), 6.88 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 143.1, 141.1, 138.9, 133.4, 130.9, 129.9, 127.5, 121.9, 121.7, 116.7. Anal. Calcd for $C_{38}H_{24}N_2O_2$: C, 84.42; H, 4.47; N, 5.18. Found: C, 84.31; H, 4.41; N, 5.26.

2. Photophysical Experiments

Absorption spectra were recorded using a HP-8453 diode array UV/Vis spectrophotometer, using 1 cm path-length quartz cuvettes. The steady state emission spectra were measured using a PTI QM-4CW system, equipped with a R298 photomultiplier tube. Delayed phosphorescent emission spectra were measured using a gated analog detector with R928 red extended PMT in toluene at 77 K. Variable high rep rate pulsed xenon source for excitation was used in the gated phosphorescent spectral measurements. The absorption spectra of ADBP, ACBP, and DABP are shown in Figure S-1a. The fluorescent and phosphorescent spectra of ADBP, ACBP, and DABP are shown in Figure S-1b, S-1c, and S-1d respectively.

Quantum yields were measured at room temperature in a dichloromethane solution. A screw-sealed 1 cm quartz cuvette was used for measurements. A solution of quinine sulfate dihydrate in 1 N H_2SO_4 was used as a reference.

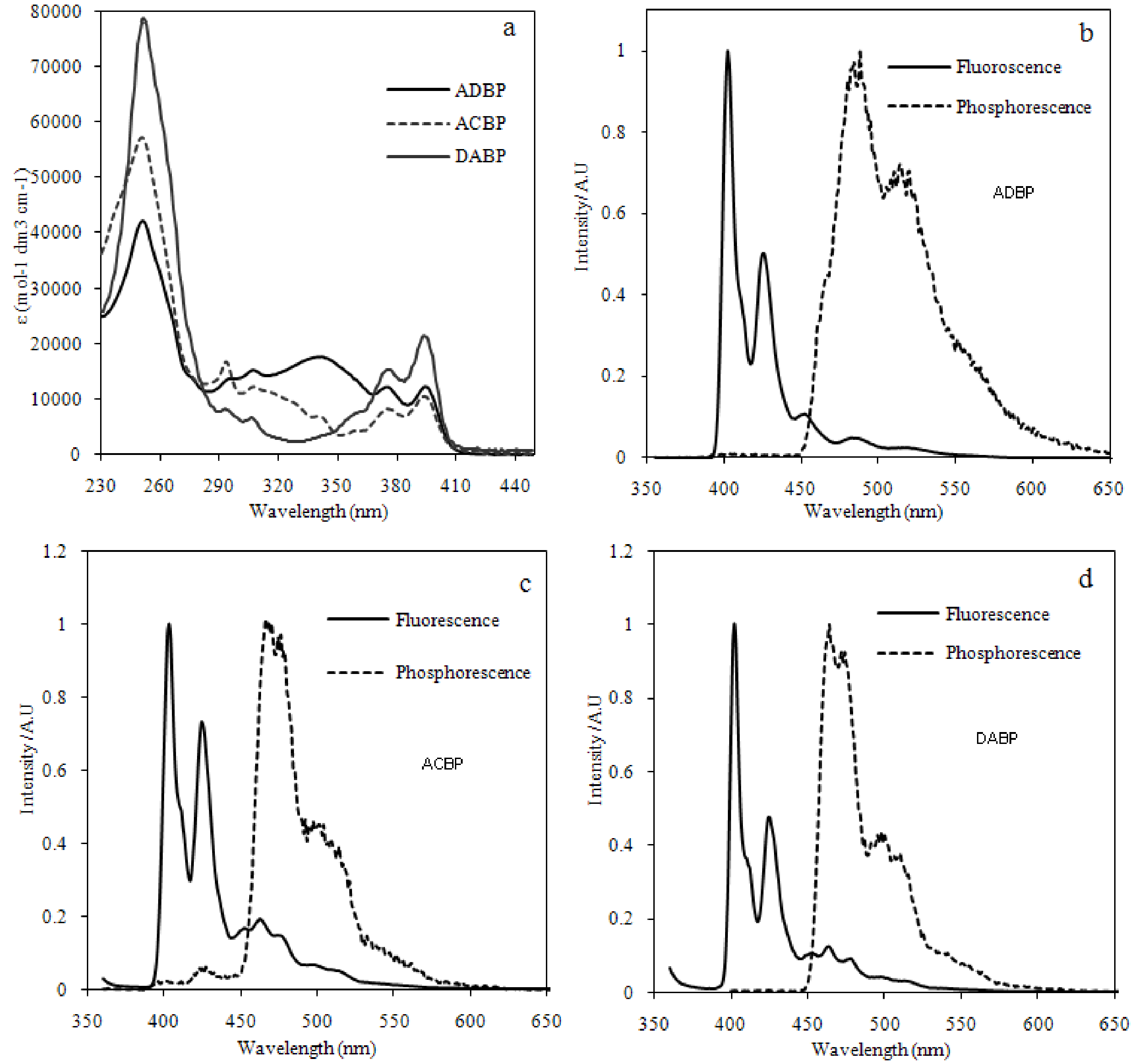


Figure S-1. Absorption spectra recorded in dichloromethane (a). Fluorescent and phosphorescent emission spectra recorded in toluene at 77 K (b: ADBP; c: ACBP; d: DABP).

3. Electrochemical Experiments

A Model CHI660 electrochemical analyzer was employed to carry out the electrochemical measurements. Cyclic voltammetry (CV) was used to characterize the redox properties of the compounds. A glassy carbon (GC) disk electrode was used as working electrode. A platinum wire served as counter electrode and a saturated calomel electrode (SCE) was used as a quasi-reference electrode to complete a standard 3-electrode electrochemical cell. Ferrocene (Fc) was used as an internal standard. Toluene-Acetonitrile (v/v: 1:1) was used as organic solvent system. The supporting electrolyte, tetrabutylammonium tetrafluoroborate (Fluka, echem grade) was used as received. All solvents used were low water grade (<20ppm water). The testing solution was purged with high purity nitrogen gas for approximately 5 minutes to remove oxygen and a nitrogen blanket was kept on the top of the solution during the course of the experiments. All measurements were performed at ambient temperature of 24±1°C.

4. Computational Details

The geometry optimizations were performed for the ground state (*S0*) and the lowest triplet state (*T*1) using density functional theory (DFT) with the B3LYP hybrid functional[3]. The 6-311G(d,p) basis set[4] was used for the optimization. The triplet energy E_T *(T1-S0)* was estimated as the difference between the total energies of the lowest triplet state (*T*1) and the ground singlet state (*S*0). All calculations were performed using Gaussian 03 program[5] installed on the Altix 4700 at East Carolina University.

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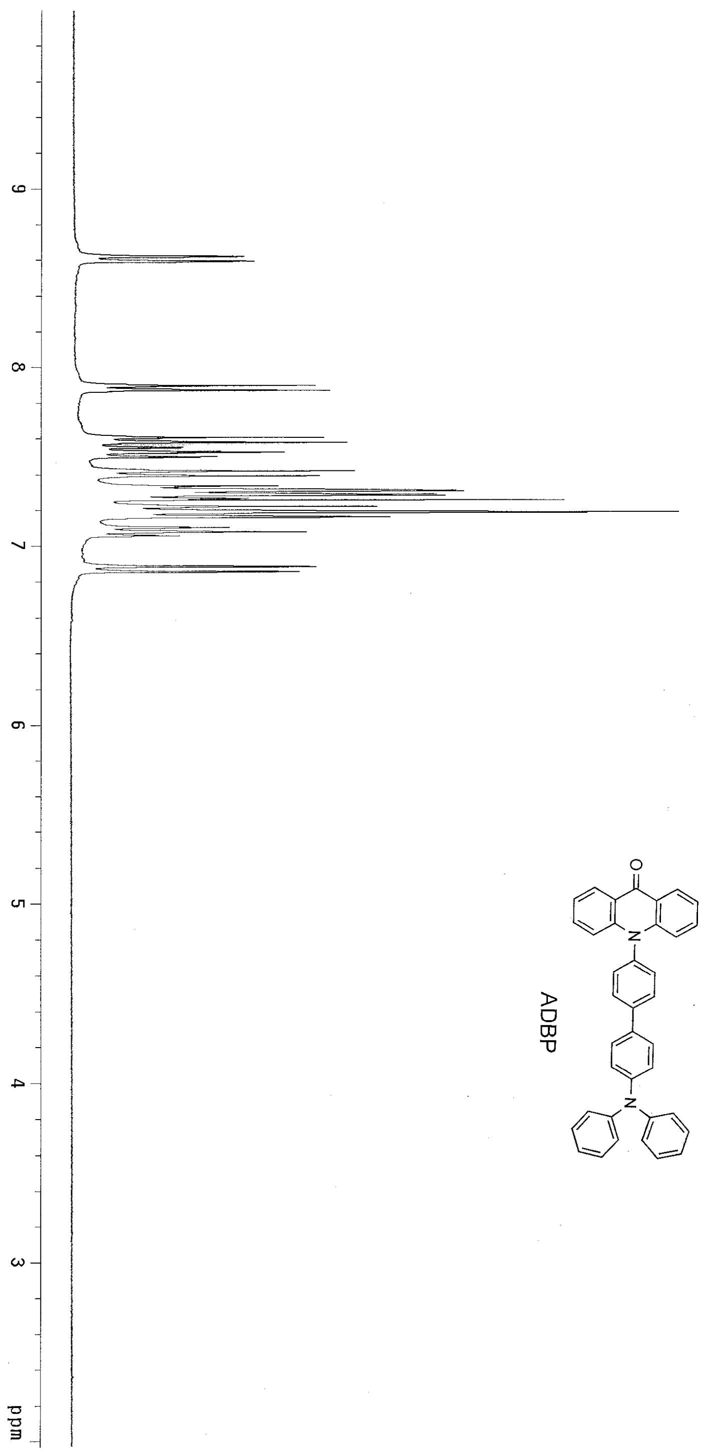
(4) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A.. *J. Chem. Phys.* **1980**, *72*, 650.

(5) *Gaussian 03, Revision C.02*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian, Inc., Wallingford CT, **2004**.

5. OLED Device Fabrication

Bottom-emitting OLEDs, were fabricated on ~1.1-mmthick glass substrates pre-coated with a transparent indium tin oxide (ITO) conductive layer having a thickness of ~22 nm and a sheet resistance of ~68 X/square. The substrates were cleaned and dried using a commercial glass scrubber tool. The ITO surface was subsequently treated with oxygen plasma, and then conditioned as a modified anode by decomposing CHF3 gas in a plasma treatment chamber to deposit an ~1-nm-thick layer of CFx. Six substrates in each experiment were then transferred into a vacuum chamber for sequential deposition of all organic and metal layers on top of the substrates by a thermal evaporation method without breaking vacuum (~10^{-6} Torr). The deposition rates and doping concentrations of materials were controlled and measured in situ using calibrated thickness monitors. The deposition rate of the organic host materials was ~0.4 nm/s, and the deposition rates of the dopant materials were adjusted according to the volume ratio in the host materials. The Al cathode formed on top of the organic layers has a thickness of about 210 nm. Each OLED has an emission area of 1 mm^2. The devices were transferred from the vacuum chamber into a nitrogen-filled glove box for encapsulation before testing. The EL characteristics of all the fabricated devices were evaluated using a constant current source (Keithley 2400 SourceMeter) and a photometer (Photo Research SpectraScan PR 650) at room temperature. The external quantum efficiencies (EQE) of the devices were calculated with the assumption of a Lambertian angular distribution of light emitted from the devices.

6. NMR spectra of ADBP, ACBP, and DABP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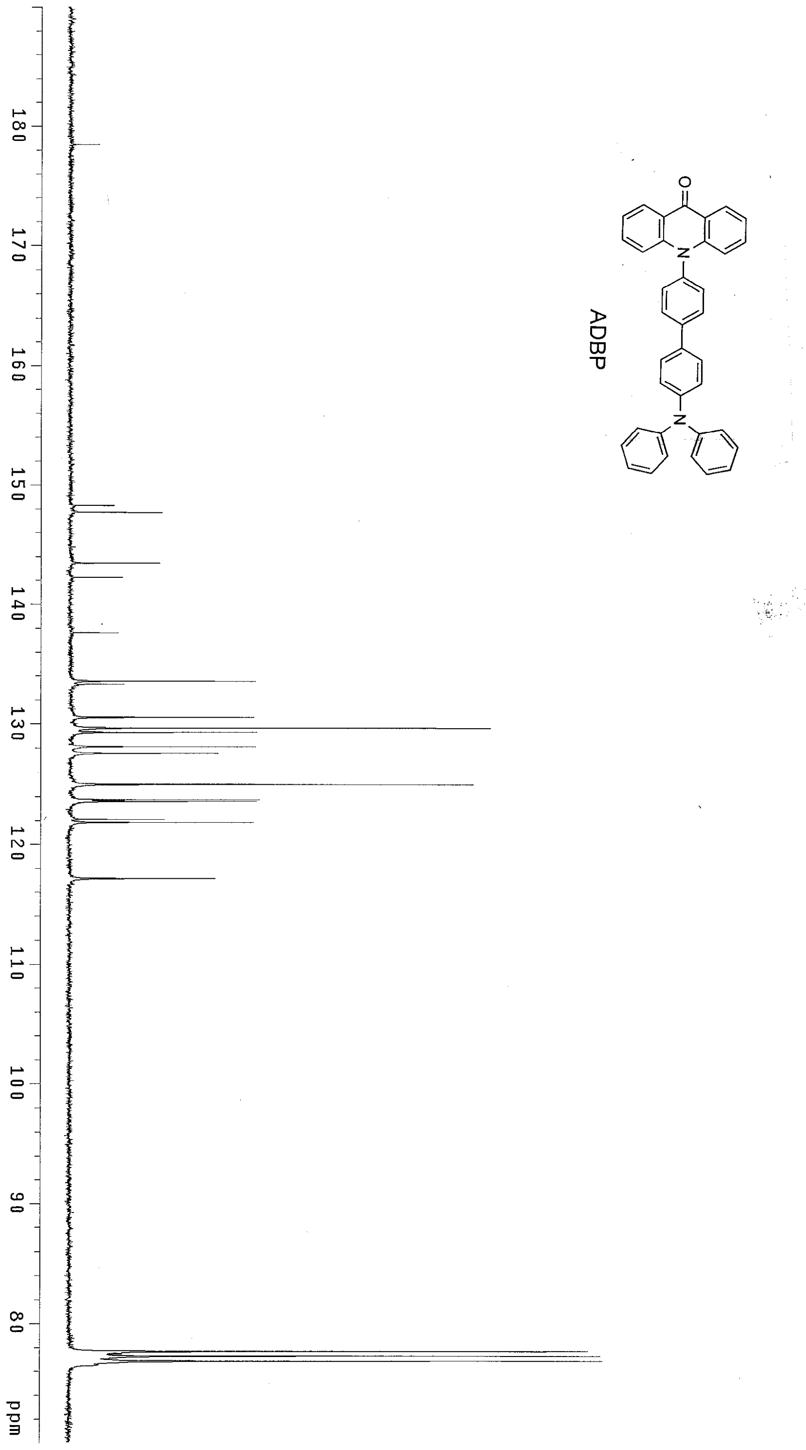
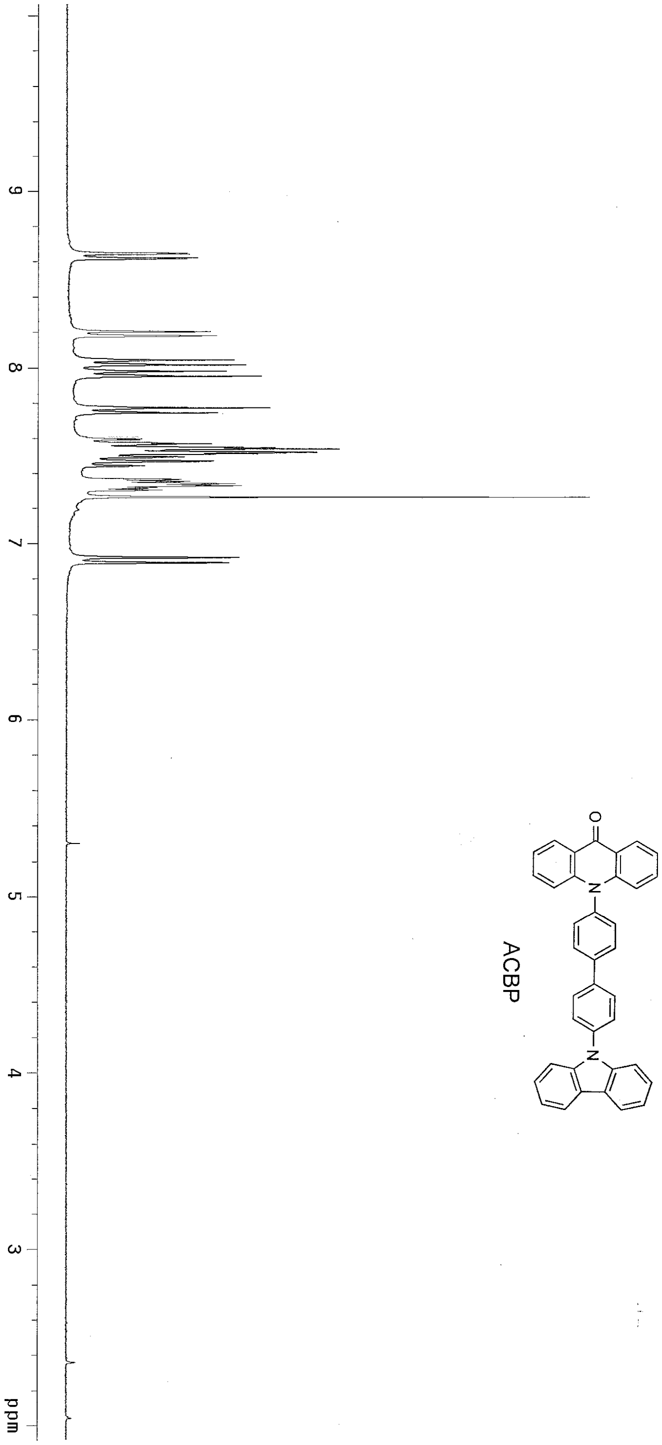


ADBP



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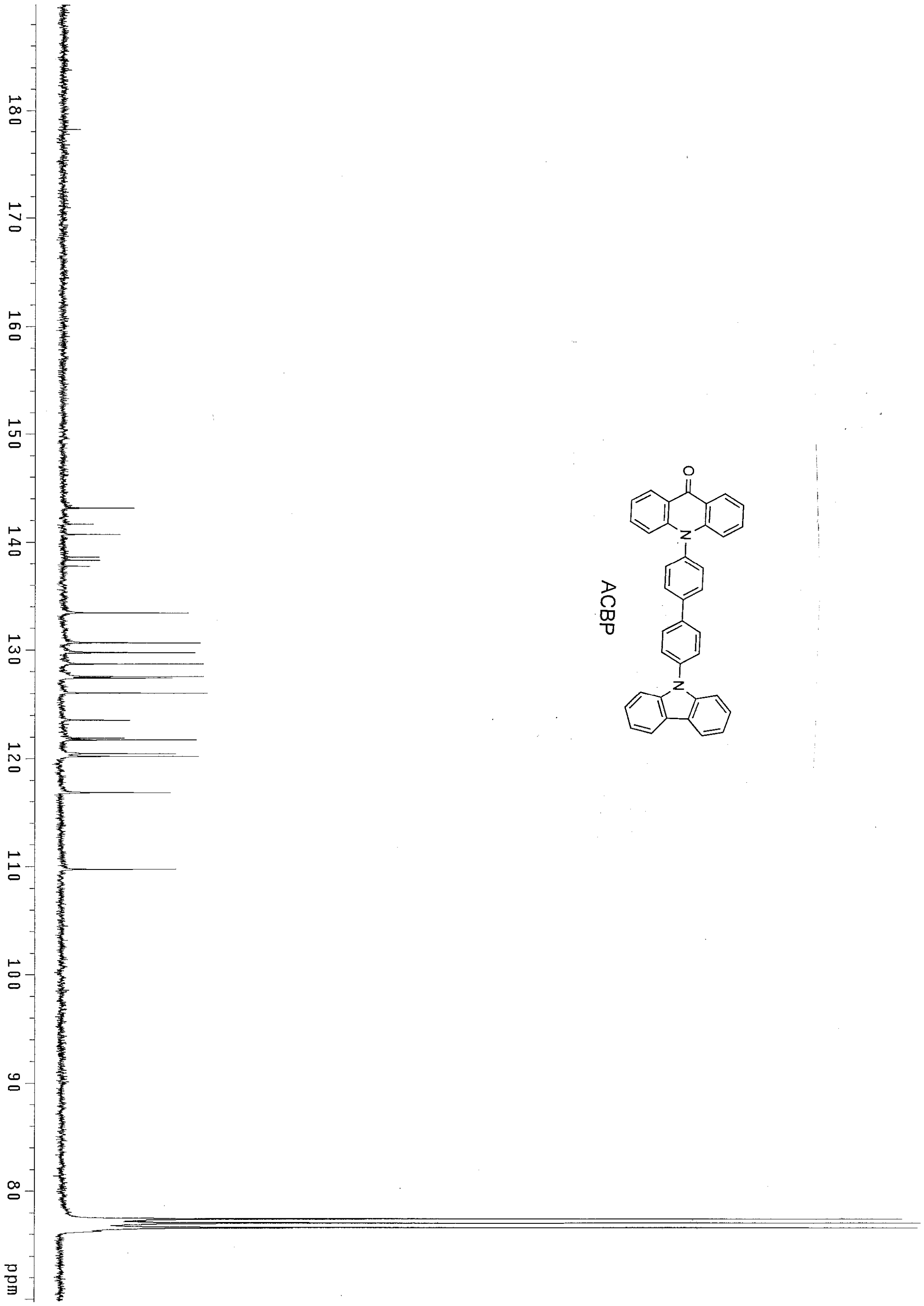

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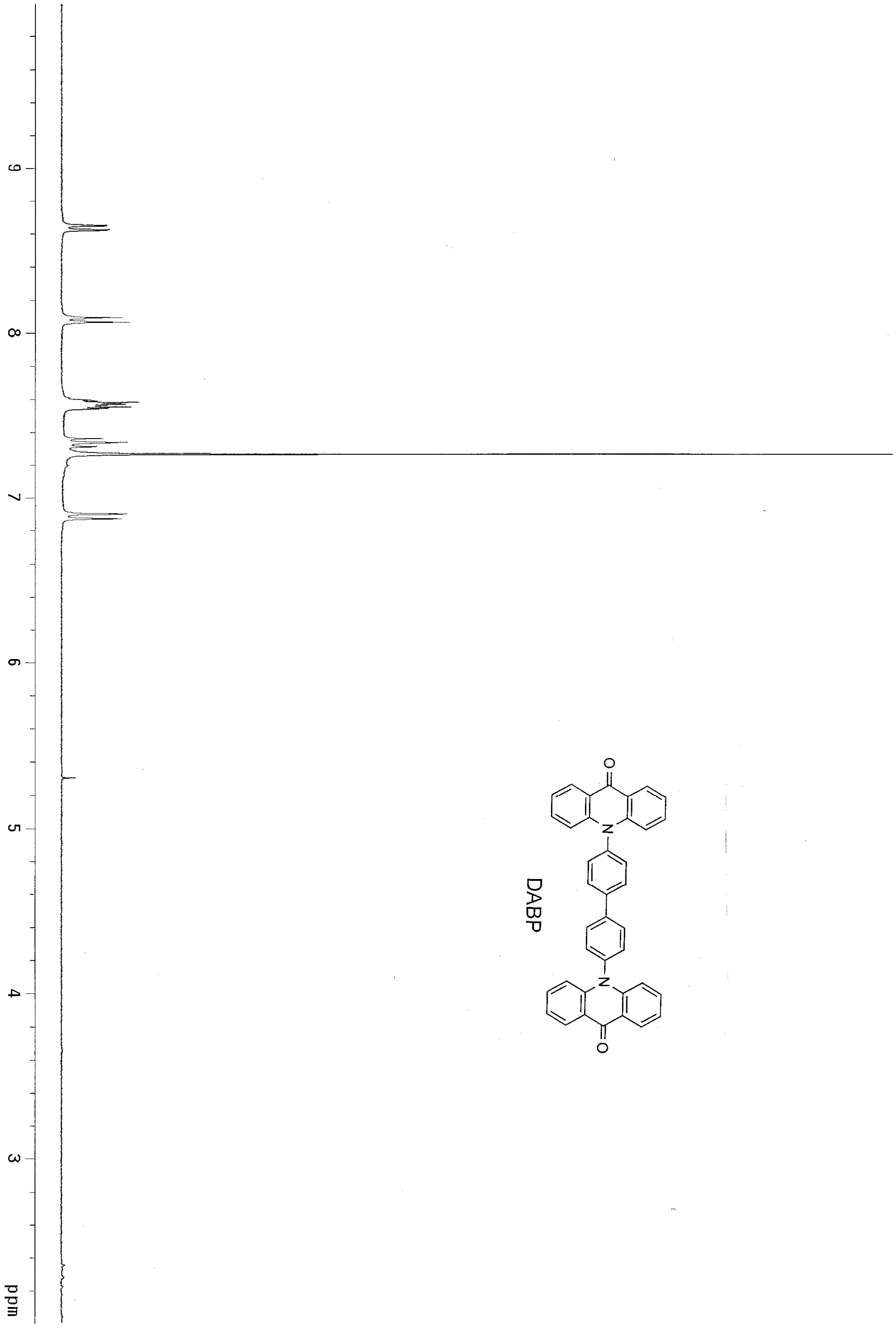
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DABP
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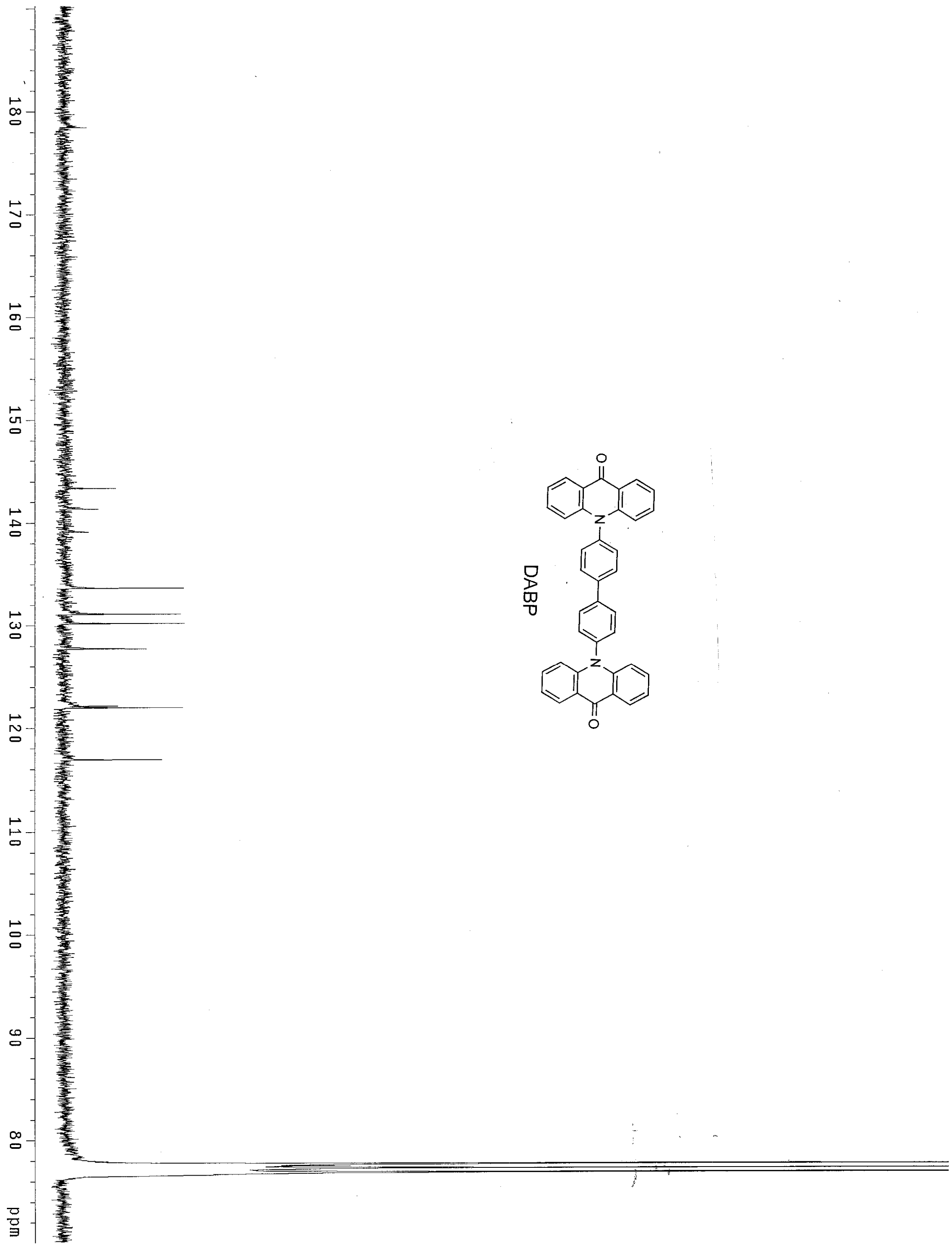
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