Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
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Supporting Information

Synthesis of Novel Triarylamine-Based Dendrimers with N^4,N^6-Dibutyl-1,3,5-Triazine-4,6-Diamine Probe for Electron/Energy Transfers in H-Bonded Donor-Acceptor-Donor Triads and as Efficient Cu^{2+} Sensors

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Experimental section

General Information

All anhydrous reactions were carried out by standard procedures under nitrogen atmosphere to avoid moisture. The solvents were dried by distillation over appropriate drying agents. Reactions were monitored by TLC plates and column chromatography was generally performed on silica gel. ^{1}H and ^{13}C NMR were recorded on a 300 MHz spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz and relative to TMS (0.00) for ^{1}H and ^{13}C R, (s, d, t, q, m, and br means single, double, ternary, quadruple, multiple, and broad single, respectively), and d-chloroform (7.26) & (77.0) was used as references for 1H and 13C NMR, respectively. Mass spectra (MALDI and FAB) were obtained on the respective mass spectrometers. Elemental analysis was carried out by Elemental Vario EL. FT-ATR spectra were measured by using Perkin Elmer spectrum 100 series spectrometer. Spectra were collected at a resolution of 4 cm^{-1} using a deuterated triglycine sulfate detector by averaging four scans. Absorption and fluorescence spectra were measured on V-670 Spectrophotometer and F-4500 Fluorescence Spectrophotometer, respectively. X-ray diffraction studies of the glass substrates were performed using monochromatic CuKα 1 radiation. Fargo Mp-2D melting point apparatus was used to measure the melting ranges of all solid compounds. Compounds **1**, **3**, **6**, and **13** were purchased commercially from Sigma-Aldrich and were proceeded for the further reactions. Compounds **5**, **7**, **8**, and ^{1}**PBI** were synthesized with required purities as per the literatures. Identification and purity of the Intermediates 9-12 were characterized by NMR (1H & 13C), Mass (MALDI and FAB), and melting point measurements. Whereas the identification and purity of final dendrimers **TPAD1** and **TPAD2** were characterized by NMR (^{1}H & ^{13}C), Mass (MALDI and FAB), elemental analysis, and melting point measurements.

Donor-Acceptor-Donor (D-A-D) Supramolecular triads

Compounds **TPAD1**, **TPAD2** and **PBI** were dissolved in methylcyclohexane at 1 x 10^{-5} M, for UV/Vis and PL titrations.

Synthesis of solid (D-A-D) supramolecular triads

2 equivalents of dendrimers (**TPAD1** or **TPAD2**) and 1 equivalent of **PBI** were mixed in 5 mL of THF in a vessel with inert atmosphere and stirred at 50°C for 3 days. After complete evaporation of the solvent, it was dried in vacuum at 35°C for 3 hours. The fine solid H-bonded complexes (supramolecular triads) were obtained and then used for X-ray diffraction (XRD) analysis as explained in the main text. The same supramolecular triads were dissolved in CH_2Cl_2 and used for FT-ATR-IR spectral measurements.

Sensor titrations

Dendrimers **TPAD1** and **TPAD2** were dissolved in THF:H_2O (4:1) at 1 x 10-5 M concentration. Li^{+}, Ag^{+}, K^{+}, Na^{+}, Cu^{+}, Cs^{+}, Ni^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Cu^{2+}, Fe^{3+} and Al^{3+} metal cations were dissolved in water medium at 1 x 10^{-4} M concentration from their respective chloro compounds, and Ag^{2+}, Mn^{2+}, Hg^{2+}, and Mg^{2+} were made from AgNO3, Mn(OAc)2, $Hg(OAc)_2$ and $MgSO_4$, respectively, in water medium at 1 x 10^{-4} M concentration. Penta methyl diethylene triamine (**PMDTA**) was dissolved in THF at 1 x 10^{-5} concentration.

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1-Bromo-4-hexyloxybenzene (2)

To a solution of 4-bromophenol (**1**) (10 g, 57.80 mmol) in acetone (120 mL), K_2CO_3 (16 g, 0.12 mol) was added and stirred for 10 min. 1-Bromohexane (10 ml, 70.88 mmol) was added into the previous mixture and refluxed for 16 hrs. Then, the mixture was filtered and then the filtrate was concentrated in vacuo and purified by column chromatography (hexane/CH_2Cl_2, 100:1 in vol.) to provide the required product **2** as a colorless oil: yield 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.8 Hz, 3H), 1.32–1.36 (m, 4H), 1.42–1.48 (m, 2H), 1.72–1.80 (m, 2H), 3.91 (t, J = 6.6 Hz, 2H), 6.76 (d, J = 9 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 14.0, 22.6, 25.6, 29.1, 31.5, 68.2, 112.5, 116.0, 132.1, 158.2.

4-(Hexyloxy) benzenamine (4)

To a solution of 4-acetamidophenol (**3**) (10 g, 66.15 mmol) in acetone (120 mL), K_2CO_3 (18.28 g, 0.13 mol) was added and stirred for 10 min. 1-Bromohexane (10 mL, 70.88 mmol) was added into the previous mixture and refluxed for 16 hrs. After completion of the reaction, the mixture was poured in to the water and stirred for 10 min, and then a white precipitate was obtained and dried in a vacuum oven at 60°C for 2 hrs. The precipitate was collected and stirred in 300 mL of hexane for 30 min to remove excess 1-bromohexane, and then filtered and dried in a vacuum oven at 60°C for 2 hrs. The dried precipitate was directly taken into the reaction vessel along with 100 mL of MeOH: con. HCl mixture (6:4 in vol.) and refluxed for 12 hrs. Then, the mixture was poured into water and the pH value was adjusted to 6-7, and extracted with AcOEt and concentrated in vacuo to afford the required product **4** as a brown solid with 92% yield. M. P: 45-47°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.6 Hz, 3H), 1.31–1.36 (m, 4H), 1.42–1.47 (m, 2H), 1.70–1.79 (m, 2H), 3.59 (br, -NH_2), 3.88 (t, J = 6.6 Hz, 2H), 6.62 (d, J = 9 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 14.0, 22.5, 25.6, 29.3, 31.5, 68.6, 115.5, 116.4, 139.5, 152.3.

Bis-(4-(hexyloxy) phenyl) amine[2] **(5)**

A mixture of compound **2** (1.5 equiv), compound **4** (1 equiv), K_2CO_3 (2 equiv), CuI (0.1 equiv), and L-proline (0.2 equiv) in 30 mL of DMSO was heated at 90°C for 24-30 hrs under N_2 atmosphere. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was loaded on a silica gel column and eluted with ethyl acetate/hexane (4:6 in vol.) to afford the diphenylamine compound **5** as a white solid with 84 % yield. M. P: 77-79°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.94 (t, J = 6.5 Hz, 6H), 1.36–1.53 (m, 12H), 1.74–1.83 (m, 4H), 3.94 (t, J = 6.6 Hz, 4H), 5.29 (br, -NH), 6.82 (d, J = 9 Hz, 4H), 6.93 (d, J = 9 Hz, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 14.0, 22.6, 25.7, 29.3, 31.6, 68.4, 115.4, 119.4, 137.8, 153.7.

N,N-Diphenylbenzamide[3] **(7)**

Diphenylamine (**6**) (5.076 g, 30 mmol) and pyridine (10 mL) were charged into a 50 mL-round-bottom flask. Benzoyl chloride (4.15 mL, 36 mmol) was added slowly with stirring at 0°C. The reaction mixture was warmed to room temperature and stirred to react overnight. The resulting mixture was poured into 500 mL of 10% HCl-ice-water solution and extracted with dichloromethane. The dichloromethane solution was washed with 200 mL water, 5% HCl solution, and 5% NaOH solution, successively. The solvent was evaporated to give the crude product, which was recrystallized from benzene to give off-white crystals of compound **7** with

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92% yield. M. P: 183-185°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.84-7.50 (m, 15 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 170.5, 143.8, 135.9, 130.1, 129.1, 127.7, 127.4, 126.2.

N,N-Bis-(4-bromophenyl) benzamide[3] (8)

Compound **7** (2.0 g, 7.3 mmol) was dissolved in dichloromethane and treated with bromine (0.82 mL, 16.2 mmol). The mixture was stirred at 40°C for 8 hrs and monitored by TLC until completion. The crude product was recrystallized from absolute ethanol to give the pure product **8** with 90% yield as white solid; M. P: 145-148°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46-7.23 (m, 9 H), 7.03 (d, 4 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 170.1, 142.4, 135.0, 132.2, 130.5, 128.9, 128.7, 127.9, 119.9.

General procedure for palladium catalyzed amination[4] for compounds 9 and 11

To a two neck reaction vessel equipped with a condenser, compound **8** (500 mg, 1.15 mmol), bis (4-(hexyloxy) phenyl) amine (**5**) (943 mg, 2.55 mmol), Pd $(OAc)_2$ (5.2 mg, 0.023 mmol), tri-*tert*-butylphosphine (9.4 mg, 0.046 mmol), and anhydrous toluene (30 mL) were added. The reaction mixture was degassed and refilled with nitrogen three times. The reaction mixture was refluxed for 3 days under nitrogen atmosphere and monitored by TLC. After completion of the reaction, the mixture was poured in to 300 ml DCM and filtered through celite plug to remove the undissolved inorganic materials. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate (8:2 in vol.)) to give pure product **9**. Compound **11** was also synthesized by applying the same procedure.

N,N-Bis (4-(bis (4-(hexyloxy) phenyl) amino) phenyl) benzamide (9)

Yield 72 %; white powder; M. P: 78-80°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.0 Hz, 12H), 1.29–1.50 (m, 24H), 1.74–1.84 (m, 8H), 3.94 (t, J = 6.6 Hz, 4H), 6.82 (d, J = 9 Hz, 12H), 6.95 (d, J = 9 Hz, 12H), 7.25-7.29 (m,3H), 7.46-7.49 (d, J =8.1 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 14.3, 22.9, 26.0, 29.6, 31.9, 68.5, 115.6, 120.6, 126.9, 127.9, 128.0, 128.2, 129.3, 136.4, 136.9, 140.8, 147.1,155.7, 170.7.; m/z (FAB) 1008 (M+, 100%).

N,N-Bis(4-(bis(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)amino)phenyl)benzamide (11)

Yield 64 %; brown solid; M. P: 75-77°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.0 Hz, 24H), 1.28 - 1.53 (m, 48H), 1.75 -1.84 (m, 16H), 3.95 (t, J = 6.6 Hz, 16H), 6.81 - 7.08 (m,56H), 7.20-7.30 (m,3H), 7.46-7.49 (d, J =7.8 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 14.3, 22.9, 26.0, 29.6, 31.9, 68.5, 115.4, 121.4, 122.3, 126.6, 126.8, 127.9, 129.3, 129.4, 136.9, 140.8, 141.3, 144.8, 146.7, 155.4, 170.7.; m/z (Maldi-Tof) 2077.27 (M+, 100%).

General procedure of Claisen's base benzoyl deprotection to afford compounds 10 and 12

Claisen's alkali was prepared by following a literature procedure[2]. Potassium hydroxide (9.00 g) was dissolved in 6.0 mL of water and diluted to 25 mL with methanol. Compound **9** (0.500 g, 0.55 mmol) was dissolved in 25 mL of THF and added to the previous mixture. The resulting solution was refluxed for 12 hr, and the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled and poured into water and extracted with ethyl acetate. The solvent was evaporated to give pure product **10**. Compound **12** was also synthesized by applying the same procedure.

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N^1-(4-(Bis (4-(hexyloxy) phenyl) amino) phenyl)-N^4, N^4-bis (4-(hexyloxy) phenyl) benzene-1, 4-diamine (10)

Yield 99 %: green solid; M. P: 69-71°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.0 Hz, 12H), 1.29–1.50 (m, 24H), 1.74–1.84 (m, 8H), 3.94 (t, J = 6.6 Hz, 4H), 5.30 (br, NH), 6.82 (d, J = 9 Hz, 12H), 6.95 (d, J = 9 Hz, 12H) ; ^{13}C NMR (300 MHz, $CDCl_3$) δ: 14.3, 22.9, 26.0, 29.6, 31.9, 68.5, 115.1, 118.8, 124.1, 125.0, 125.3, 138.2, 141.6, 154.1.; m/z (FAB) 904 (M+, 100%).

N^1-(4-(4-(Bis(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)amino)phenylamino)phenyl)-N^1-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-N^4,N^4-bis(4-(hexyloxy)phenyl)benzene-1,4-diamine(12)

Yield 99 %; dark green solid; M. P: 65-67°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.0 Hz, 24H), 1.28 - 1.53 (m, 48H), 1.75 -1.84 (m, 16H), 3.95 (t, J = 6.6 Hz, 16H), 5.34 (br, NH), 6.78 - 7.02 (m, 56H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 14.0, 22.6, 25.7, 29.3, 31.6, 68.2, 115.1, 116.5, 118.6, 119.7, 122.4, 123.7, 125.4, 129.0, 141.3, 141.8, 143.1, 154.8.; m/z (Maldi-Tof) 1973.24 (M+, 100%).

General procedures[5, 6] of compounds 14 and 15

To 1 equiv. of 2,4,6-trichloro-1,3,5-triazine (**13**) dissolved in 50 ml of THF, 1.1 equiv. of N,N-diisopropylethylamine (DIPEA) was added with constant stirring under nitrogen atmosphere and cooled to 0°C. 1 equiv. of Compound **10** dissolved in 50 ml of THF was added dropwise at 0°C for 1 hr. After completion of the addition, the reaction mixture was warmed to room temperature, and the reaction with stirring was monitored to be completed by TLC. After completion of the reaction, the resulting white precipitate was filtered off and the filtrate was evaporated under reduced pressure. The crude product was refluxed for 12 hrs with an excess amount of butylamine using a catalytic amount of sodium bicarbonate and 1,4-dioxane as a solvent. The reaction mixture was cooled and filtered to remove the inorganic catalyst and the filtrate was evaporated under reduced pressure, and then purified by column chromatography (neutral alumina, hexane/ethyl acetate (6:4 in vol.)) to give pure products **14**. Compound **15** was also synthesized by applying the same procedure.

N^2,N^2-Bis(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-N^4,N^6-dibutyl-1,3,5-triazine-2,4,6-triamine(14)

Yield 85%; white crystal; M. P: 80-82°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.6 Hz, 18H), 1.22–1.47 (m, 32H), 1.74–1.84 (m, 8H), 3.20 (br, 4H(N-CH_2)), 3.92 (t, J = 6.4 Hz, 4H), 4.87 (br, 2H (NH)), 6.78 (d, J = 9 Hz, 8H), 6.84 (d, J = 8.7 Hz, 4H),7.02 (d, J = 9 Hz, 12H) ; ^{13}C NMR (300 MHz, $CDCl_3$) δ: 13.8, 14.0, 20.0, 22.6, 25.7, 29.7, 31.6, 31.9, 40.3, 68.2, 115.1, 120.6, 126.2, 127.9, 128.3, 137.0, 140.9, 145.8, 155.1, 166.2.; m/z (FAB) 1126 (M+, 100%). Anal. Calcd for $C_{71}H_{96}N_8O_4$: C, 75.76; H, 8.60; N, 9.96. Found: C, 75.54; H, 8.62; N, 9.98.

N2,N2-Bis(4-(bis(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)amino)phenyl)-N^4,N^6-dibutyl-1,3,5-triazine-2,4,6-triamine (15)

Yield 78 %: pale white crystal; M. P: 73-75°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.6 Hz, 30H), 1.26 - 1.47 (m, 56H), 1.67 -1.81 (m, 16H), 3.15 (br, 4H(N-CH_2)), 3.92 (t, J = 6.4 Hz,

4H), 4.87 (br, 2H (NH)), 6.71 - 7.09 (m, 56H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 13.8, 14.0, 20.0, 22.7, 25.7, 29.3, 30.3, 31.6, 40.3, 68.2, 114.6, 121.5, 122.7, 125.8, 128.5, 137.0, 141.1, 143.8, 145.3, 147.8, 155.0, 157.6, 166.0.; m/z (Maldi-Tof) 2194.41 (M+, 100%). Anal. Calcd for $C_{143}H_{180}N_{12}O_8$: C, 78.25; H, 8.27; N, 7.66. Found: C, 77.98; H, 8.25; N, 7.63.

Notes and references

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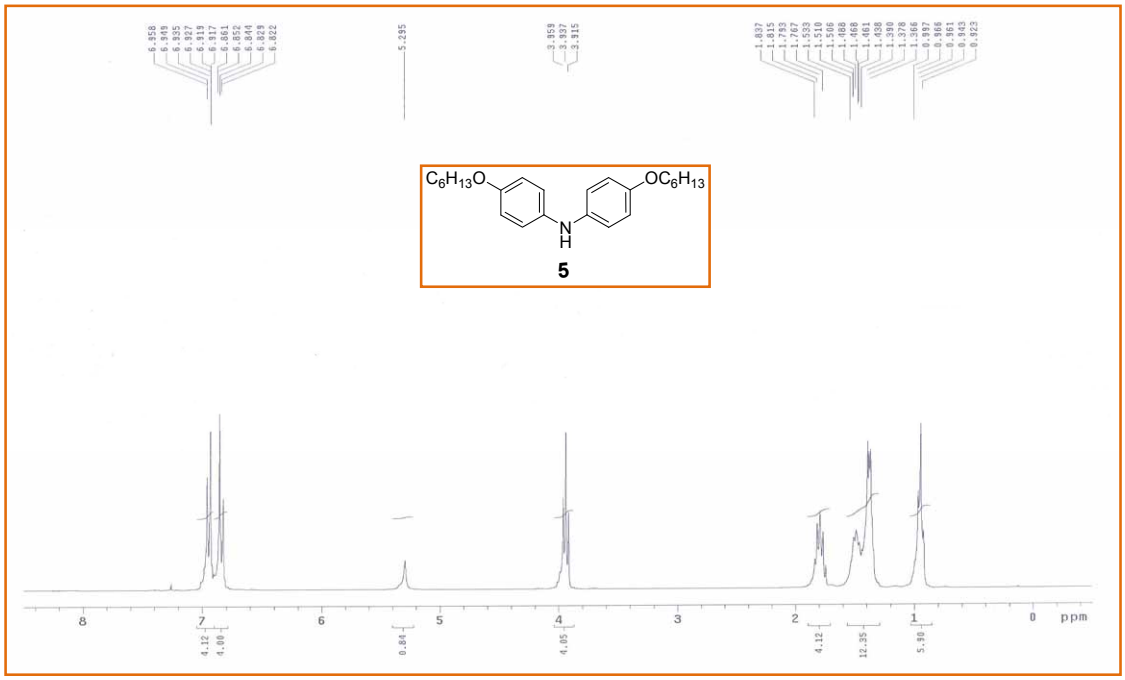

Fig. S1 ^{1}H NMR spectrum of compound **5**.

Fig. S2 ^{13}C NMR spectrum of compound **5**.

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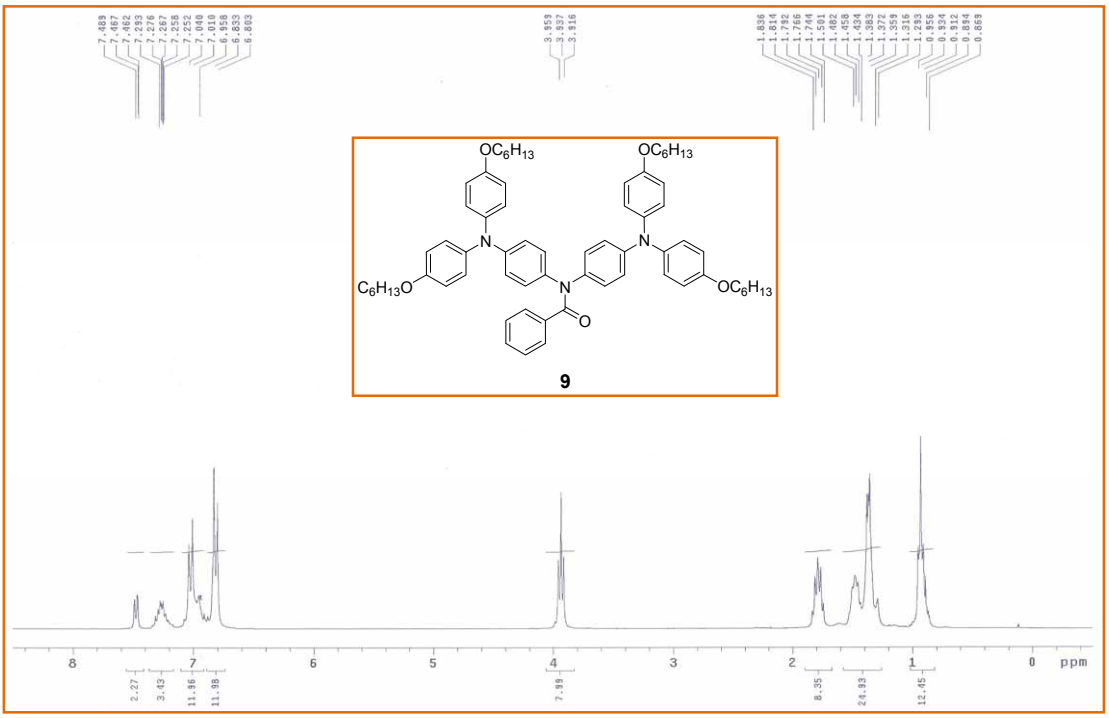

Fig. S3 ^{1}H NMR spectrum of compound **9**.

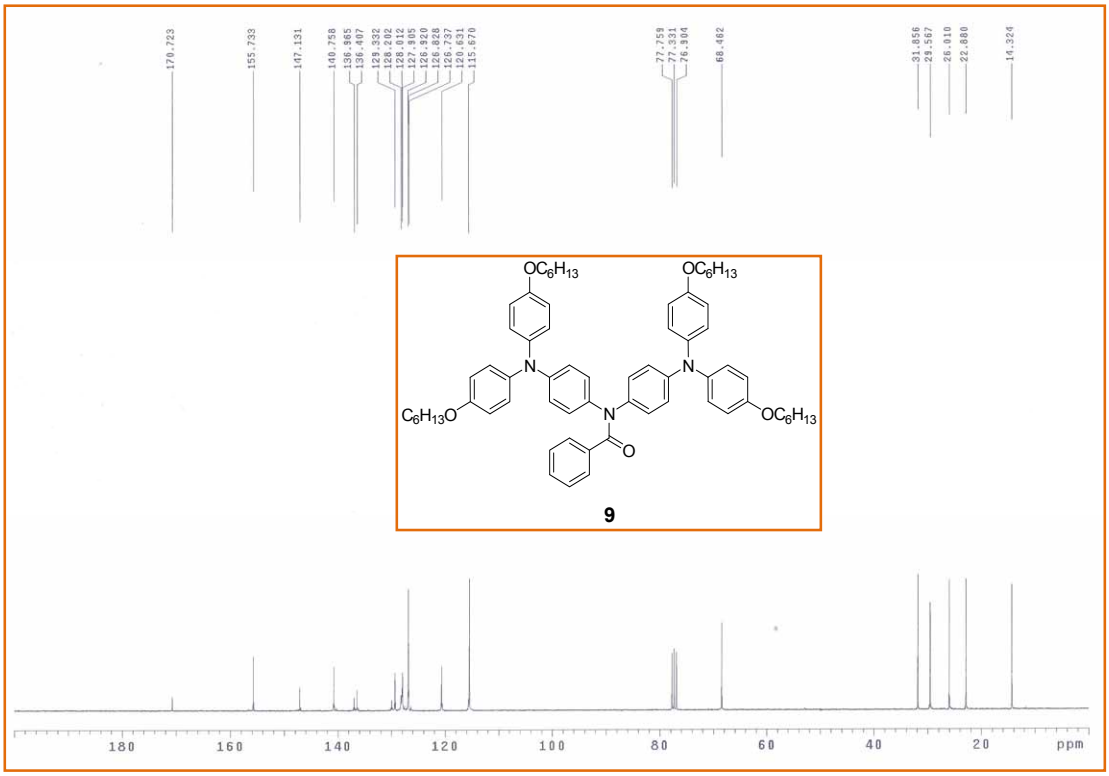

Fig. S4 ^{13}C NMR spectrum of compound **9**.

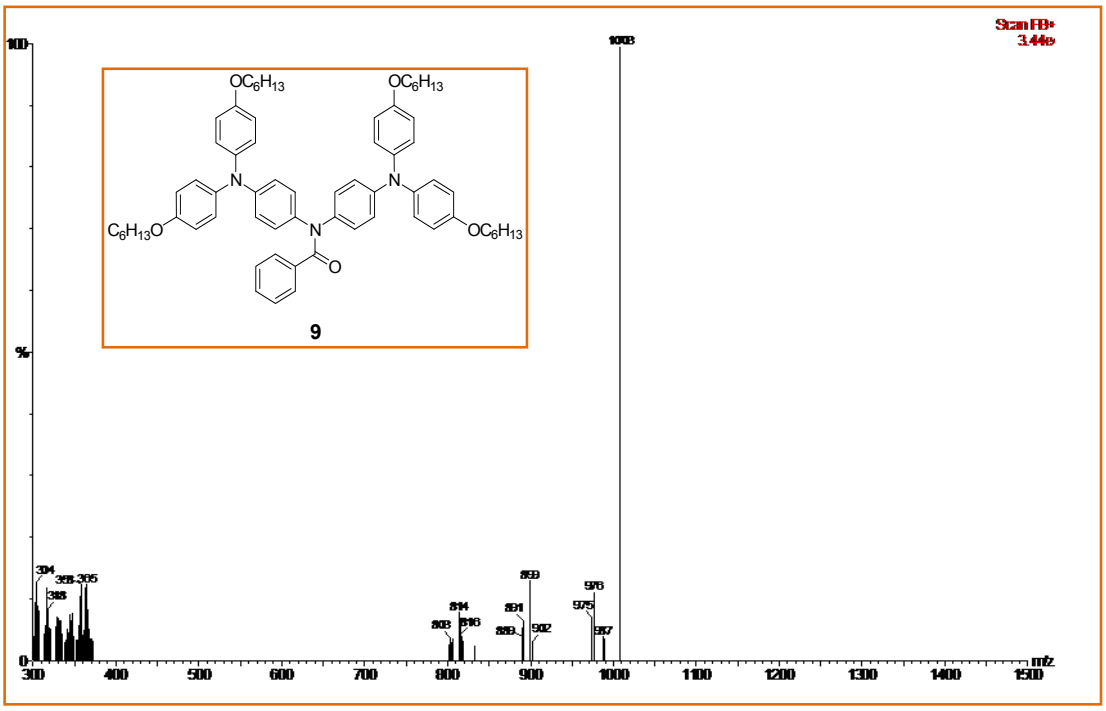

Fig. S5 Mass (FAB) spectrum of compound **9**.

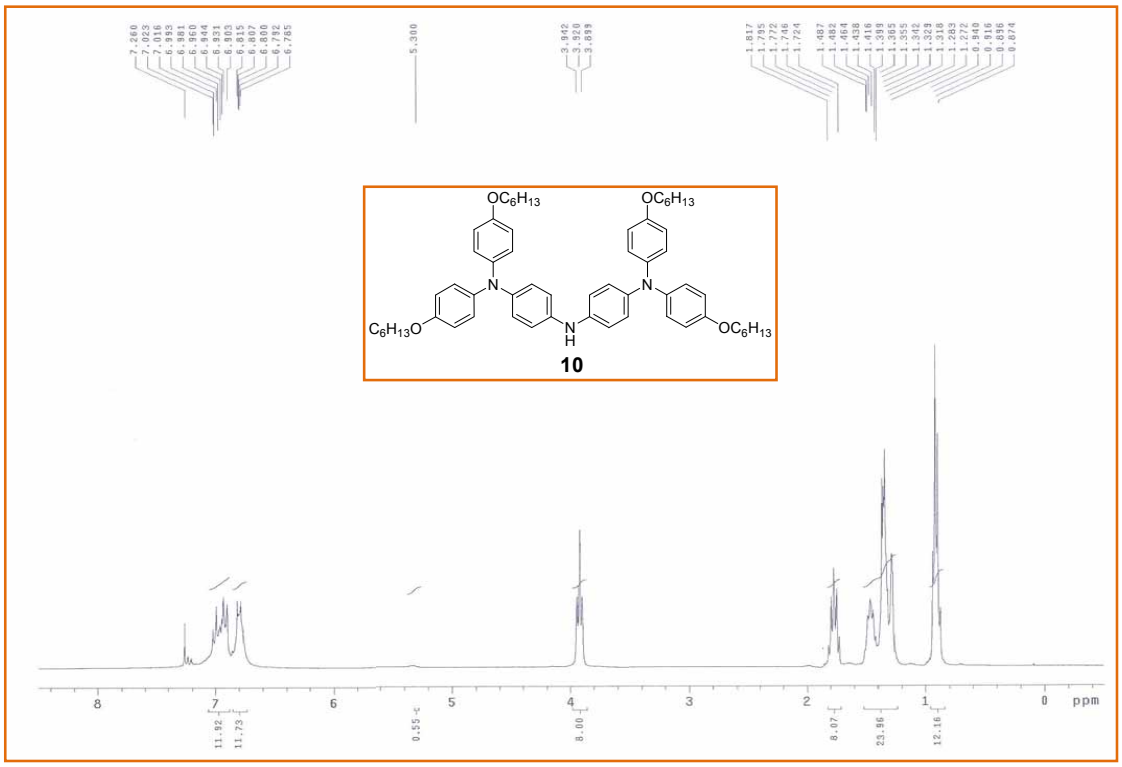

Fig. S6 ^{1}H NMR spectrum of Ccompound **10**.

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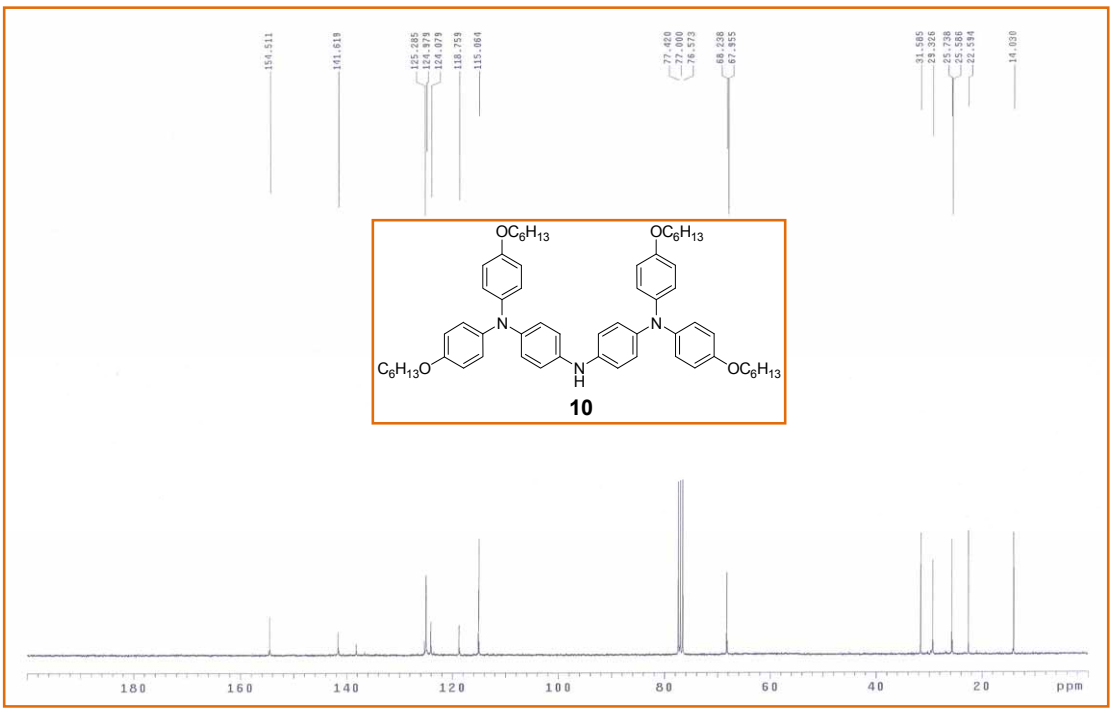

Fig. S7 ^{13}C NMR spectrum of compound **10**.

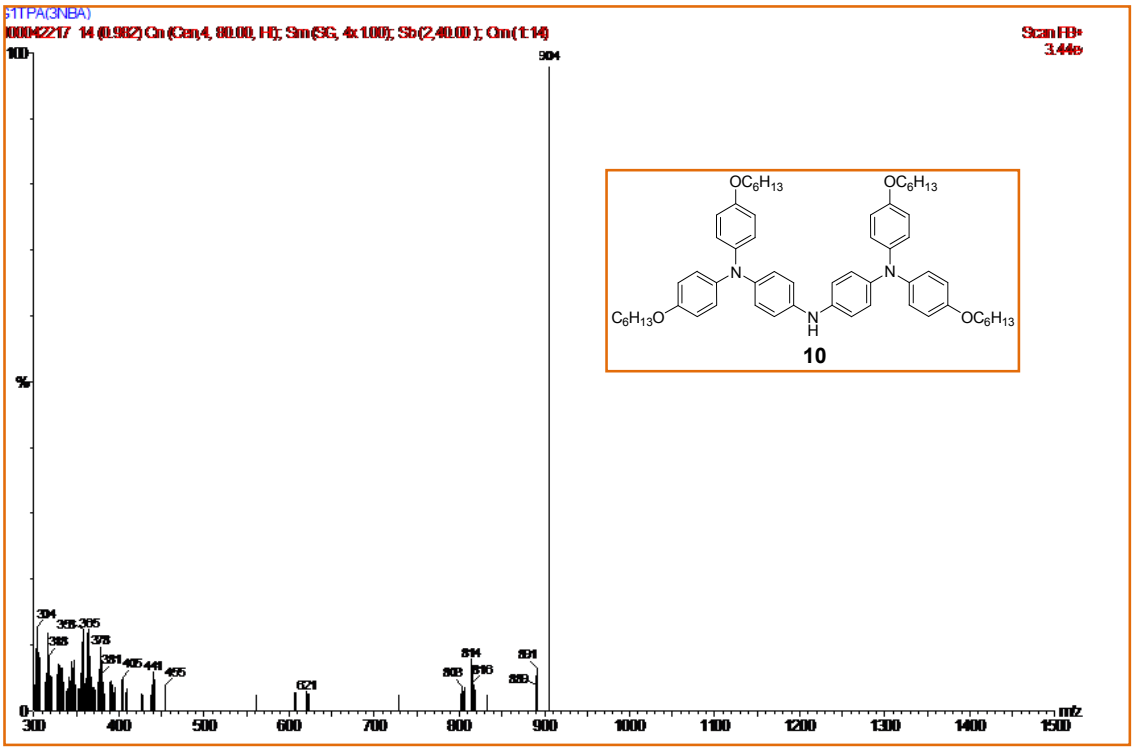

Fig. S8 Mass (FAB) spectrum of compound **10**.

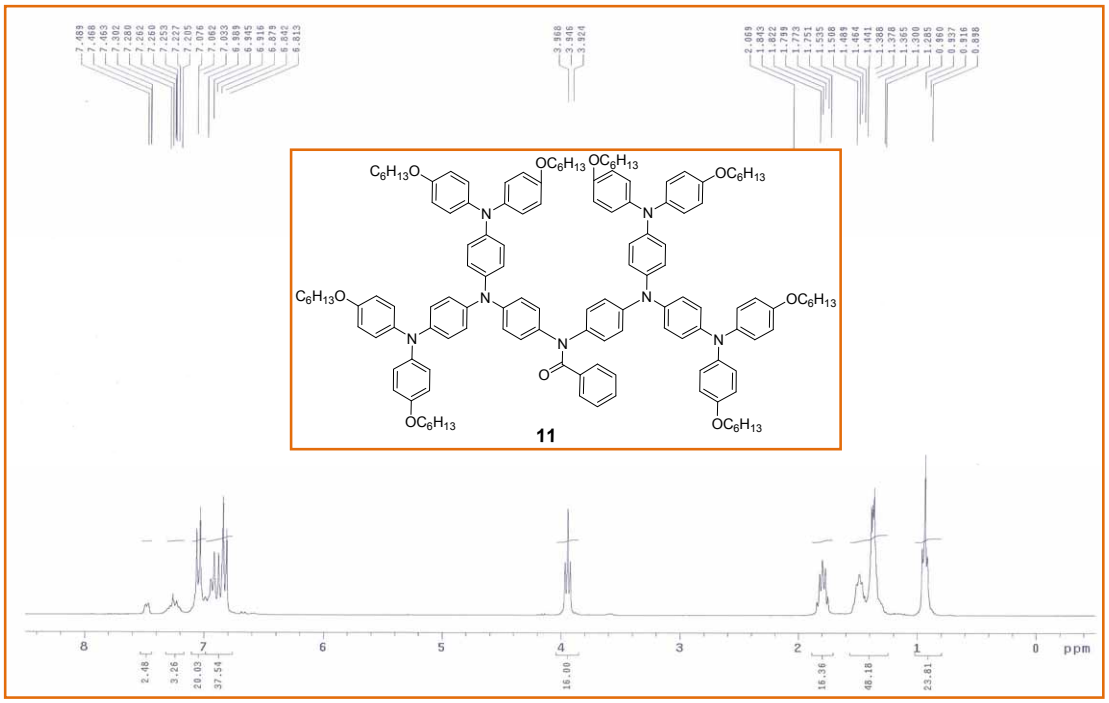

Fig. S9 ^{1}H NMR spectrum of compound **11**.

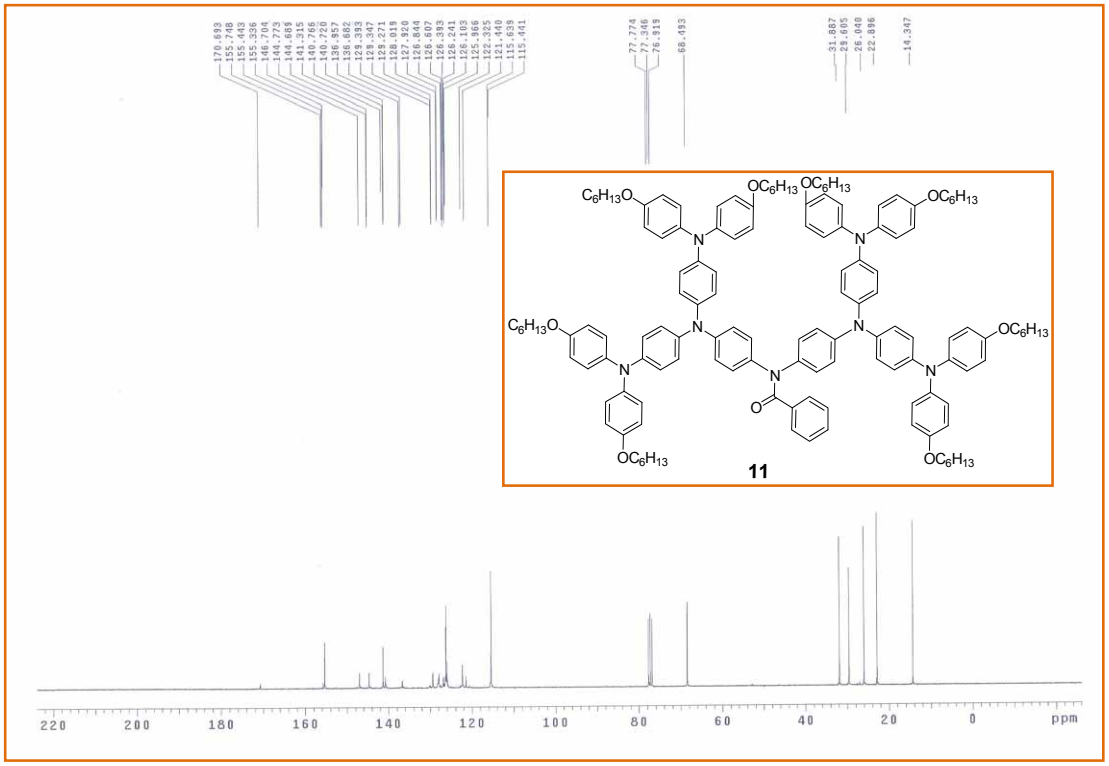

Fig. S10 ^{13}C NMR spectrum of compound **11**.

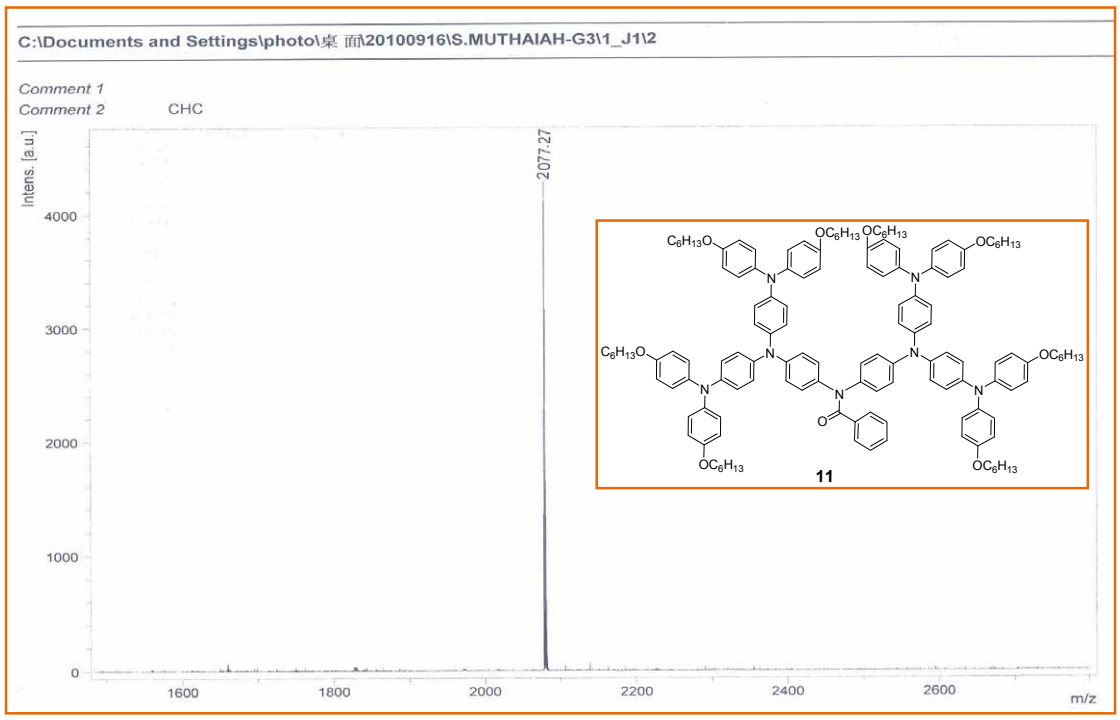

Fig. S11 Mass (Maldi-Tof) spectrum of compound **11**.

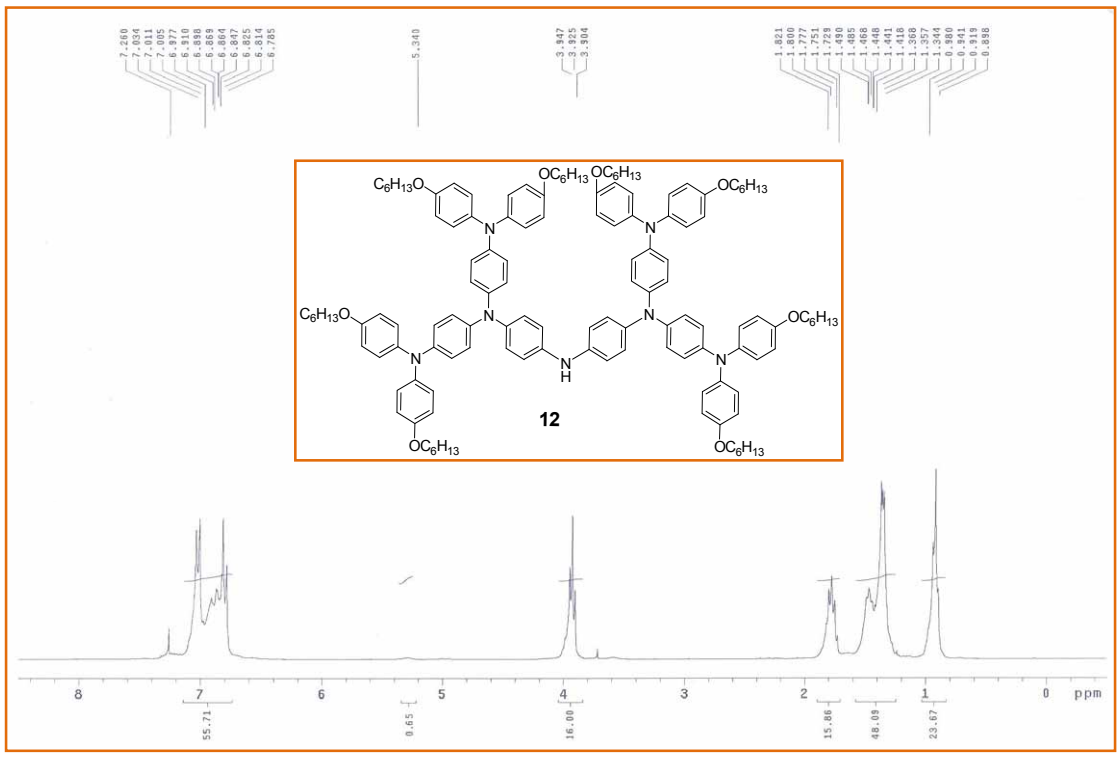

Fig. S12 ^{1}H NMR spectrum of compound **12**.

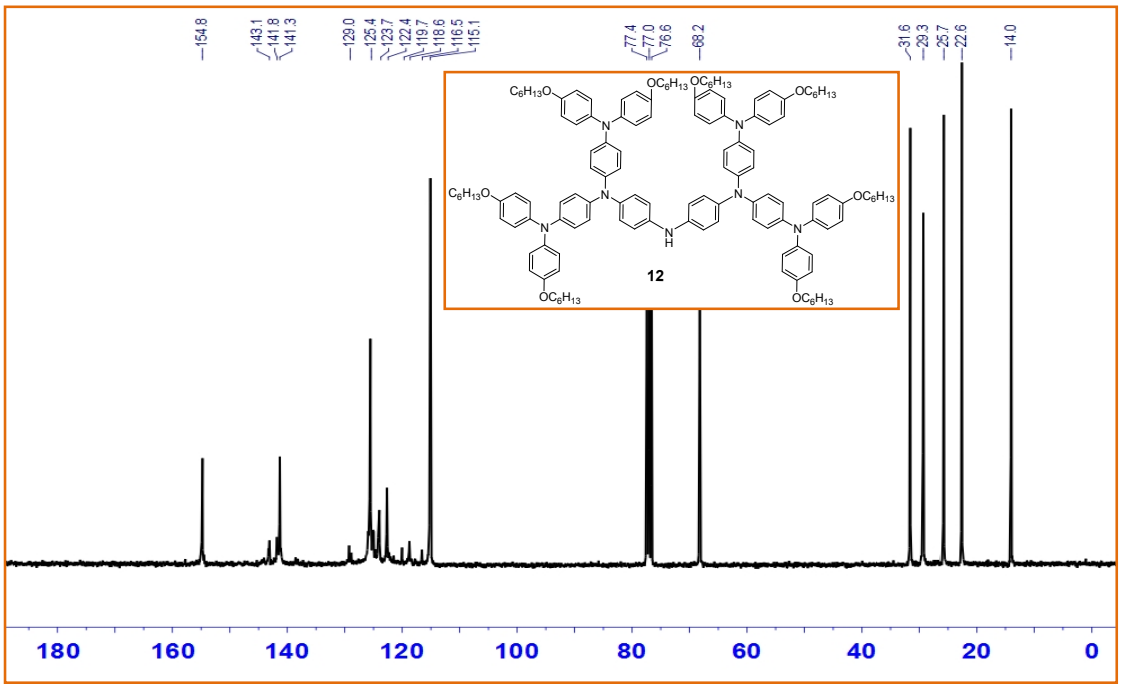

Fig. S13 ^{13}C NMR spectrum of compound **12**.

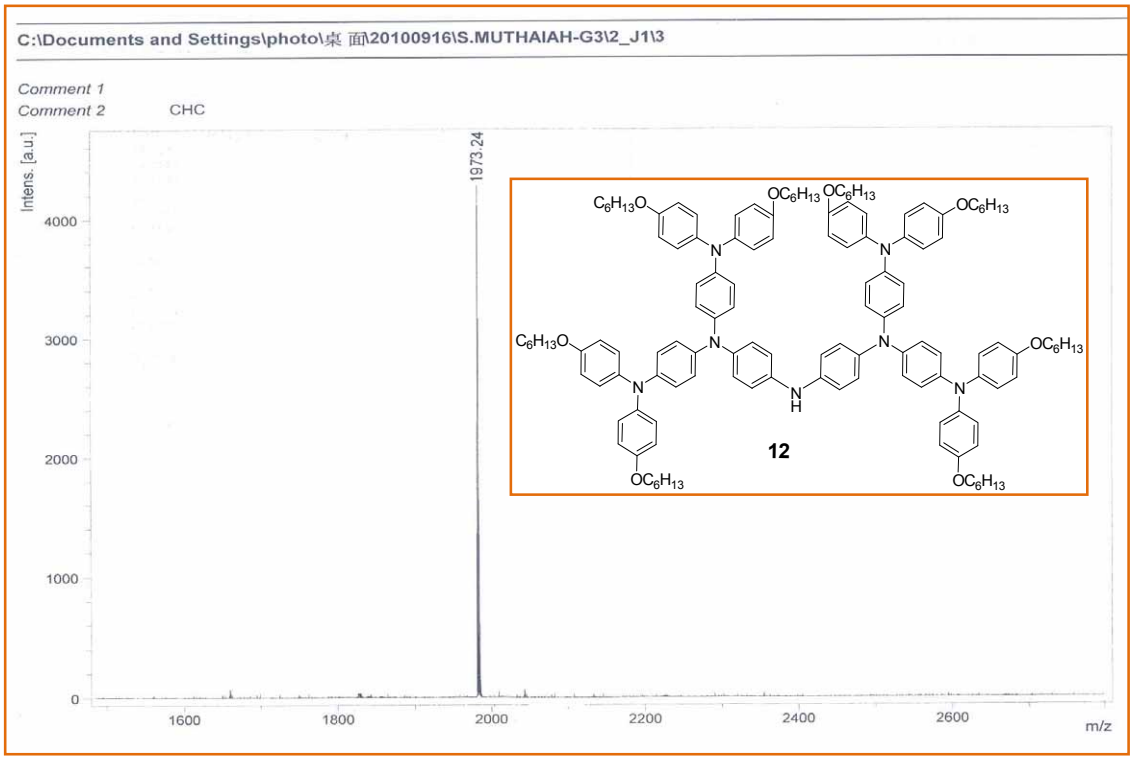

Fig. S14 Mass (Maldi-Tof) spectrum of compound **12**.

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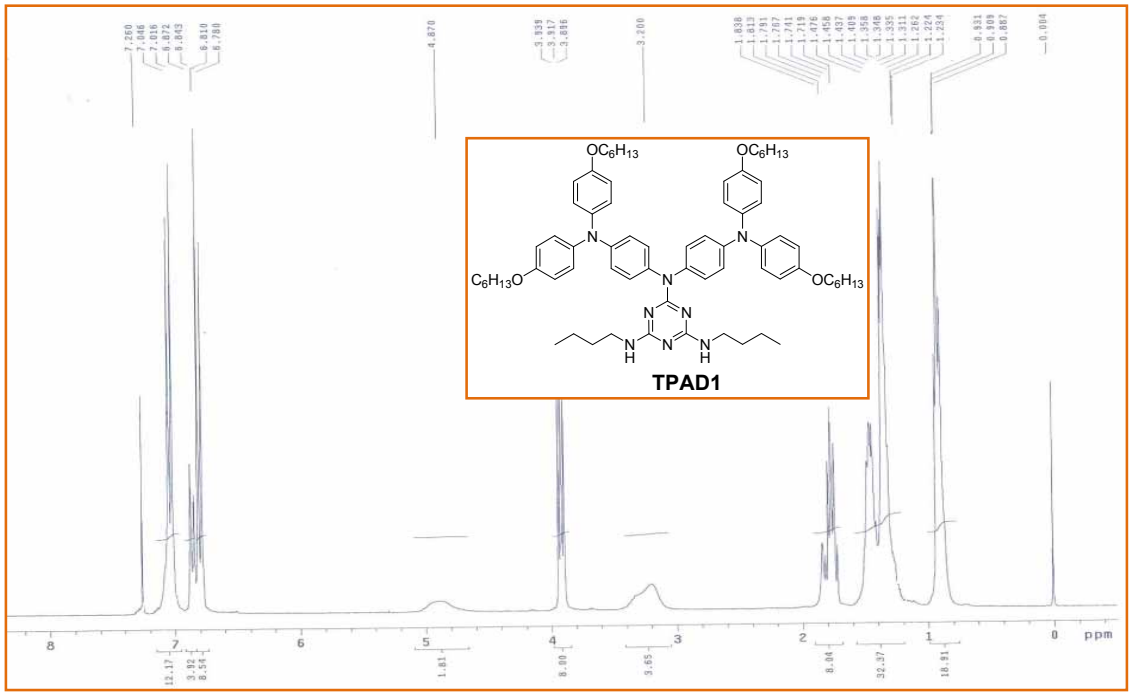

Fig. S15 ^{1}H NMR spectrum of compound **TPAD1**.

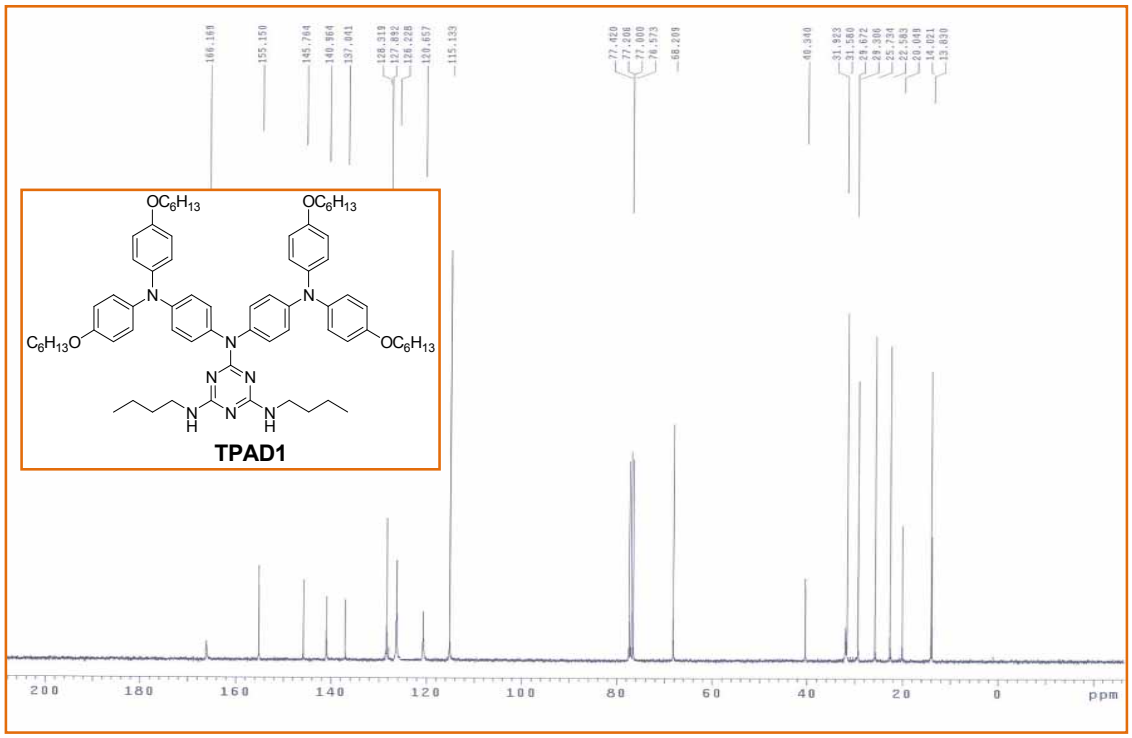

Fig. S16 ^{13}C NMR spectrum of compound **TPAD1**.

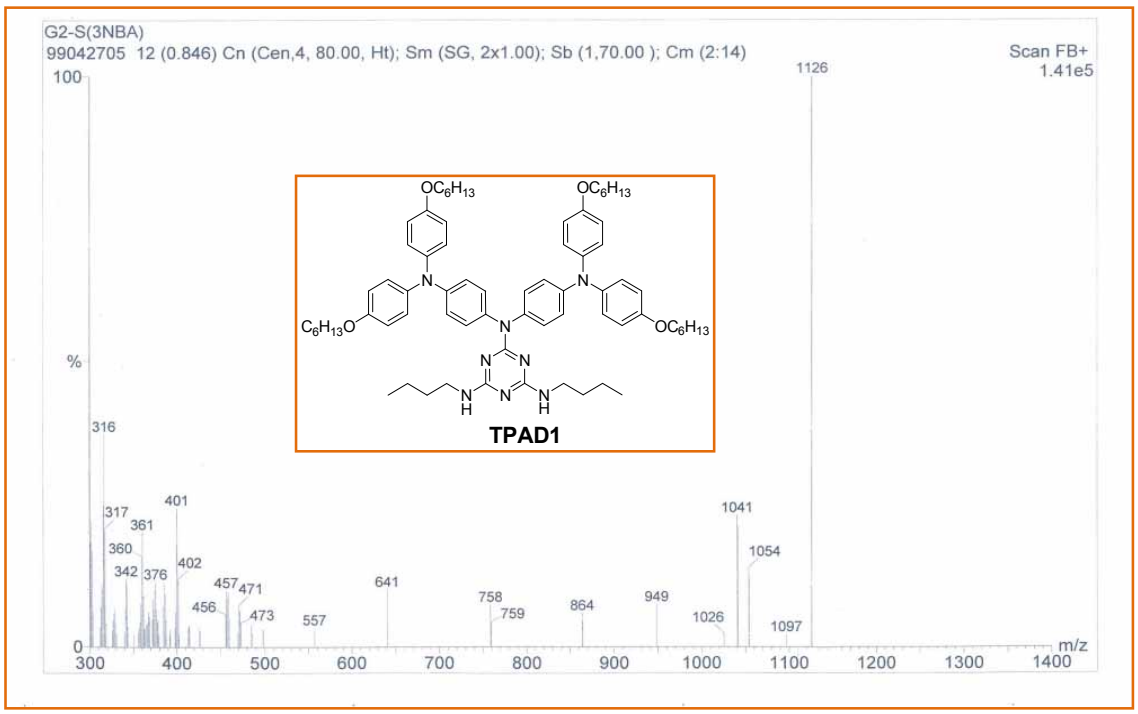

Fig. S17 Mass (FAB) spectrum of compound **TPAD1**.

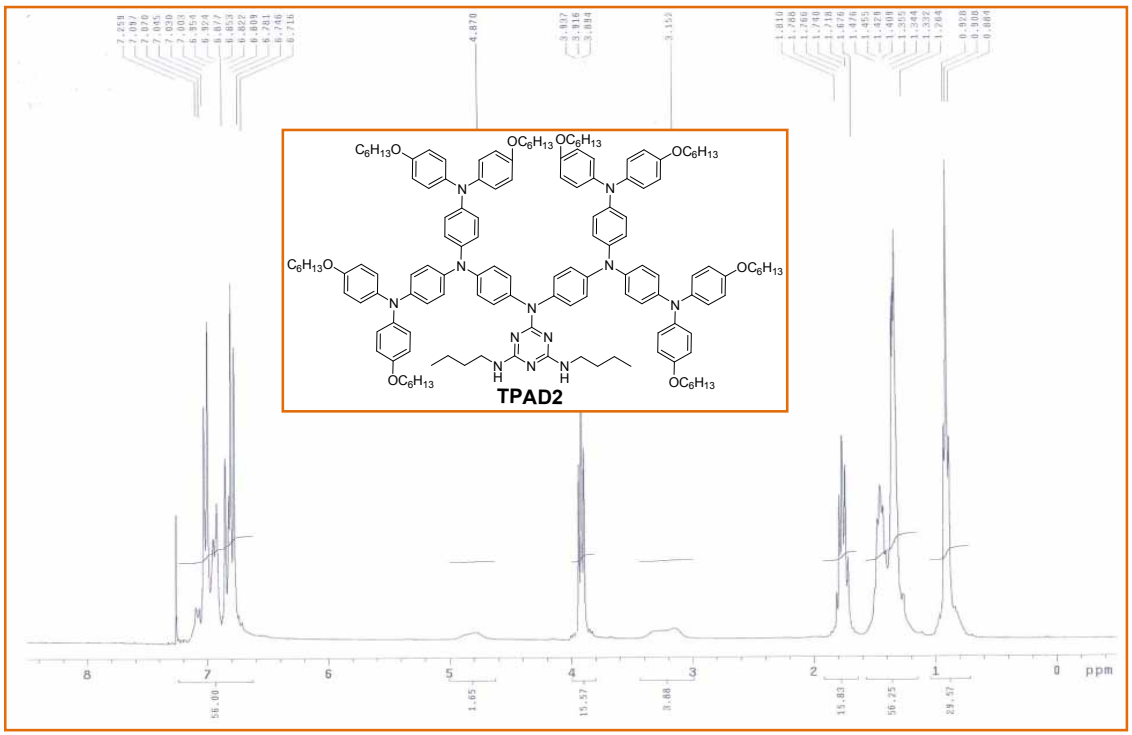

Fig. S18 ^{1}H NMR spectrum of compound **TPAD2**.

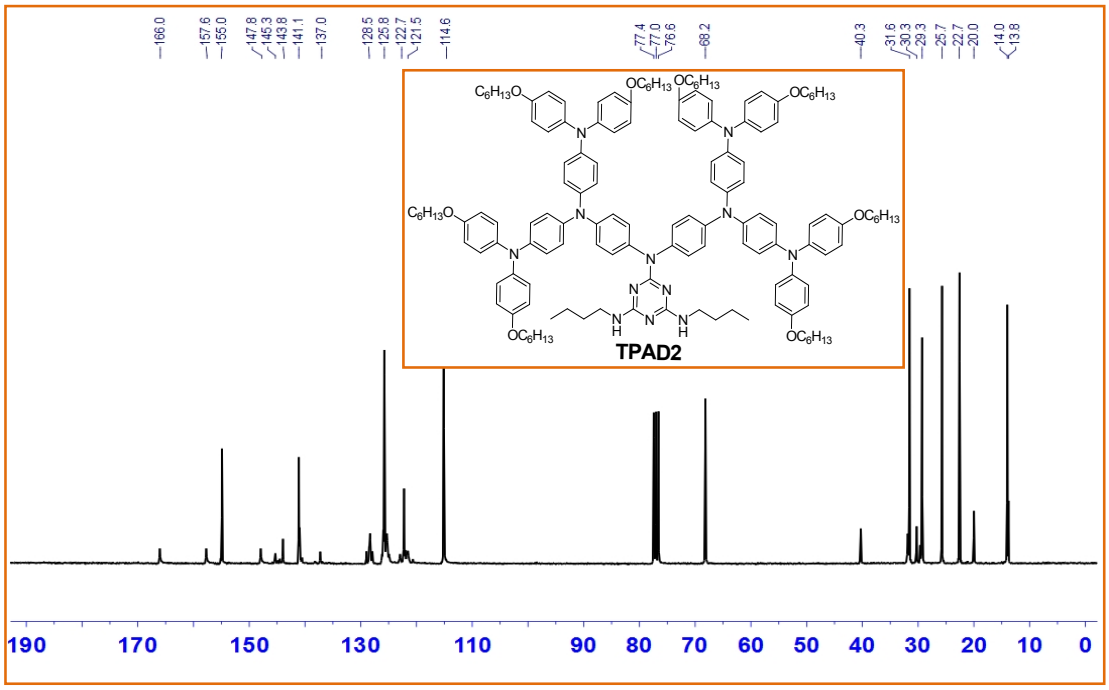

Fig. S19 ^{13}C NMR spectrum of compound **TPAD2**.

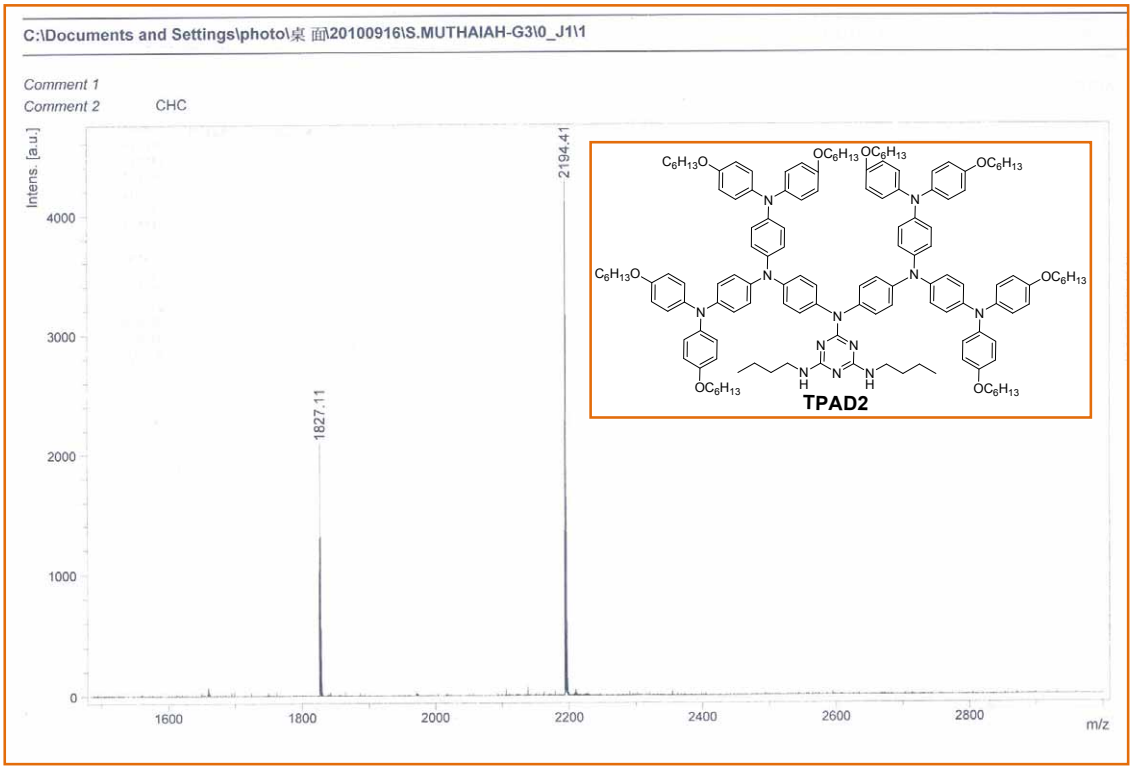

Fig. S20 Mass (Maldi-Tof) spectrum of compound **TPAD2**.

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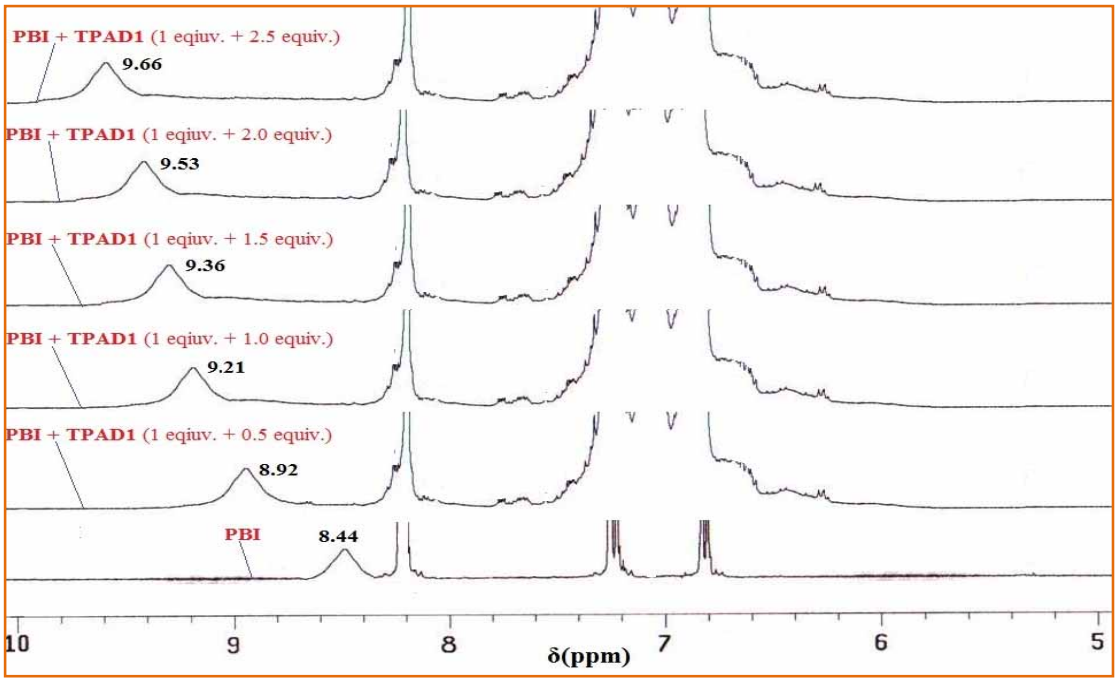

Fig. S21 ^{1}H NMR titrations of **TPAD1** (0-25mM) with **PBI** (10mM) in $CDCl_3$ at room temperature.

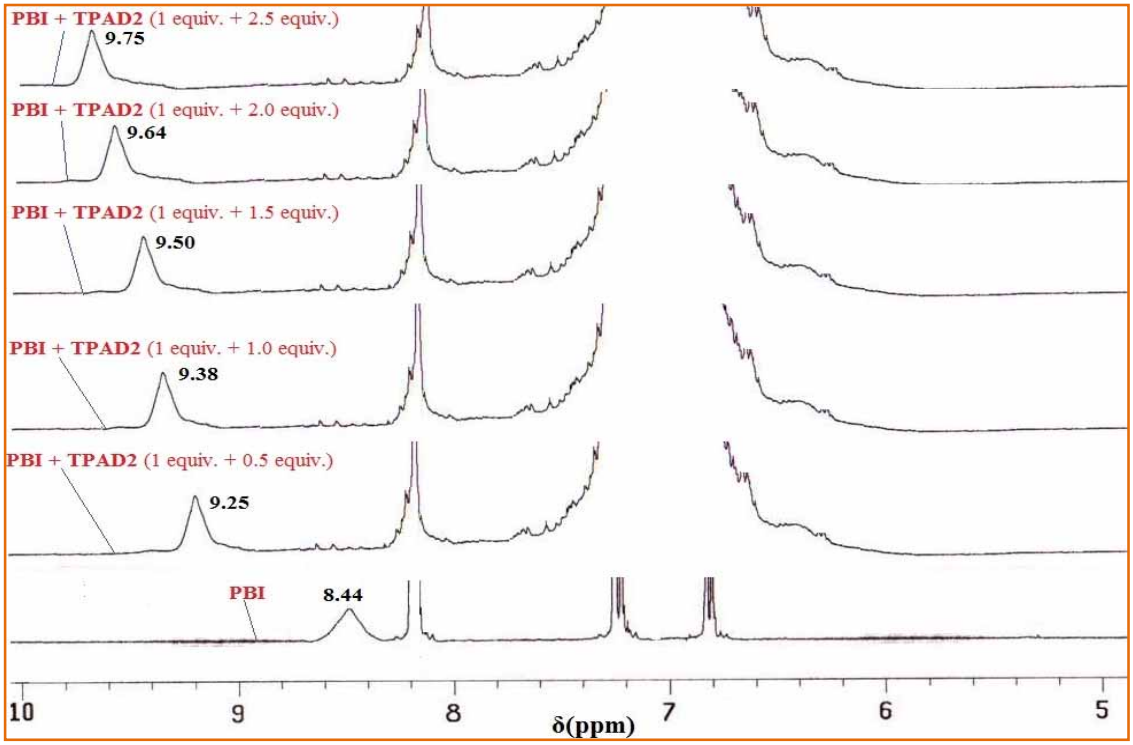

Fig. S22 ^{1}H NMR titrations of **TPAD2** (0-25mM) with **PBI** (10mM) in $CDCl_3$ at room temperature.

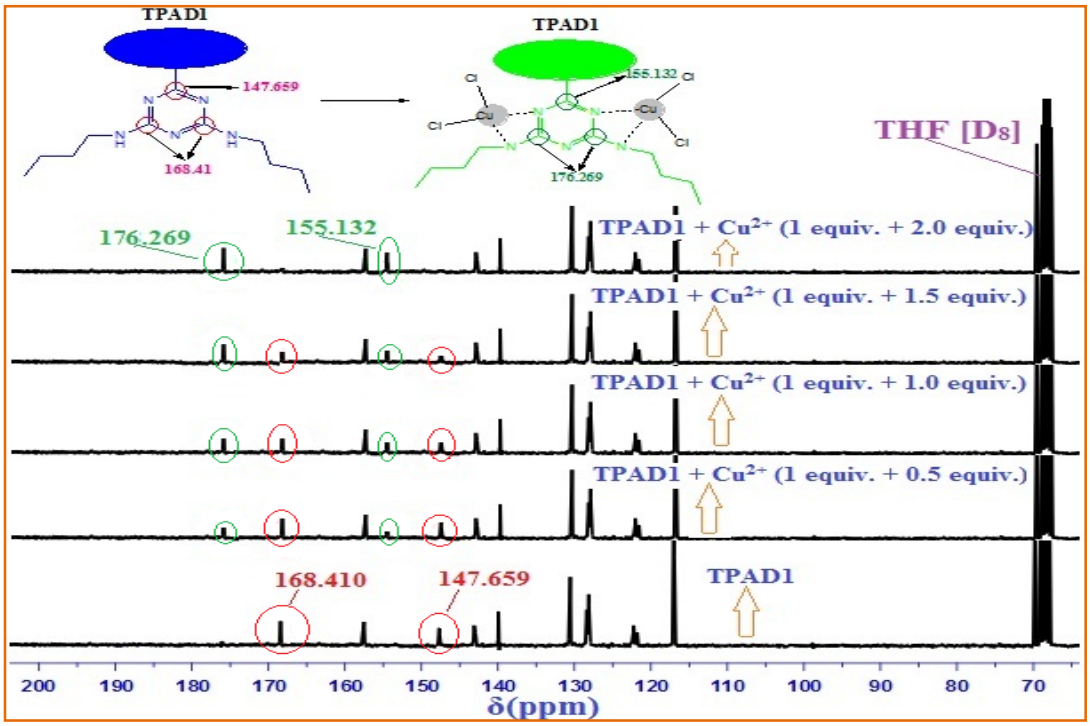

Fig. S23 ^{13}C NMR titrations of **TPAD1** in THF [D_8] (1 x 10^{-3} M) with Cu^{2+} ions (2 x 10^{-2}M) in D_2O, at room temperature and the final solvent composition is 2:1 in vol.

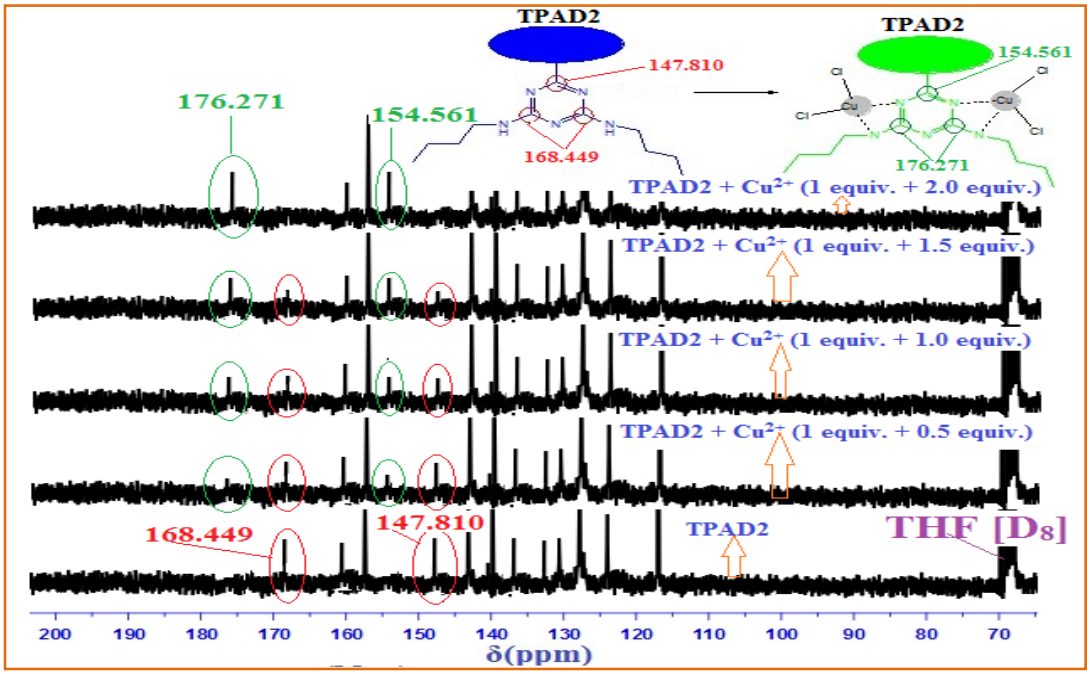

Fig. S24 ^{13}C NMR titrations of **TPAD2** in THF [D_8] (1 x 10^{-3} M) with Cu^{2+} ions (2 x 10^{-2}M) in D_2O, at room temperature and the final solvent composition is 2:1 in vol.

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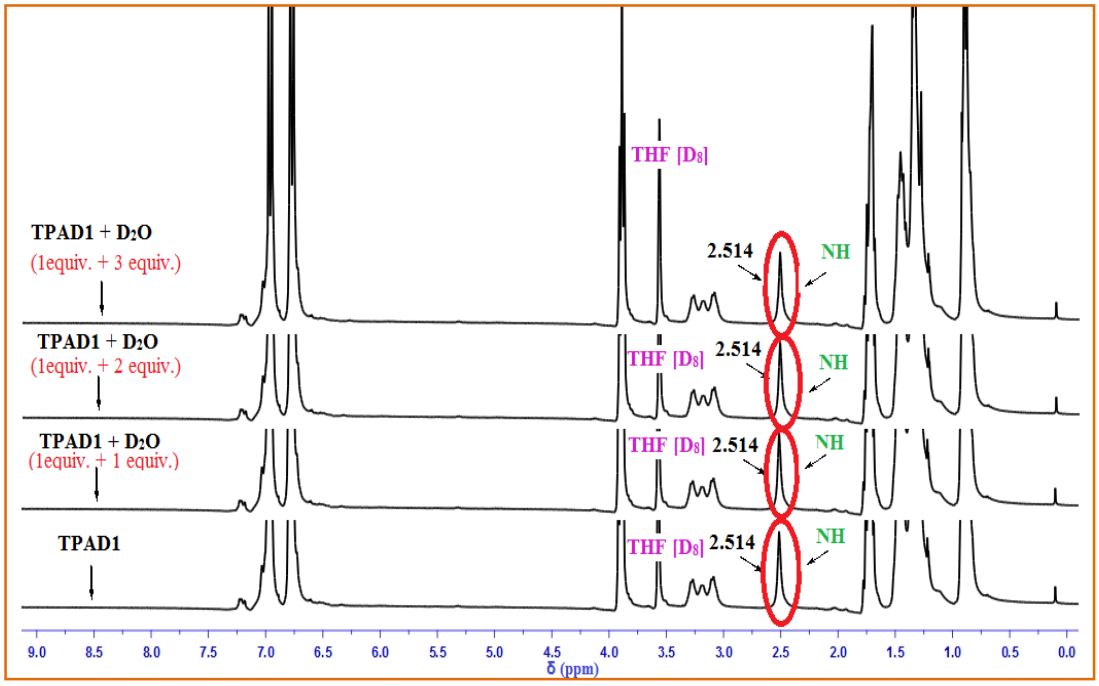

Fig. S25 ^{1}H NMR titrations of **TPAD1** in THF [D_8] with **D_2O**, at room temperature and the final solvent composition is 3:1 in vol.

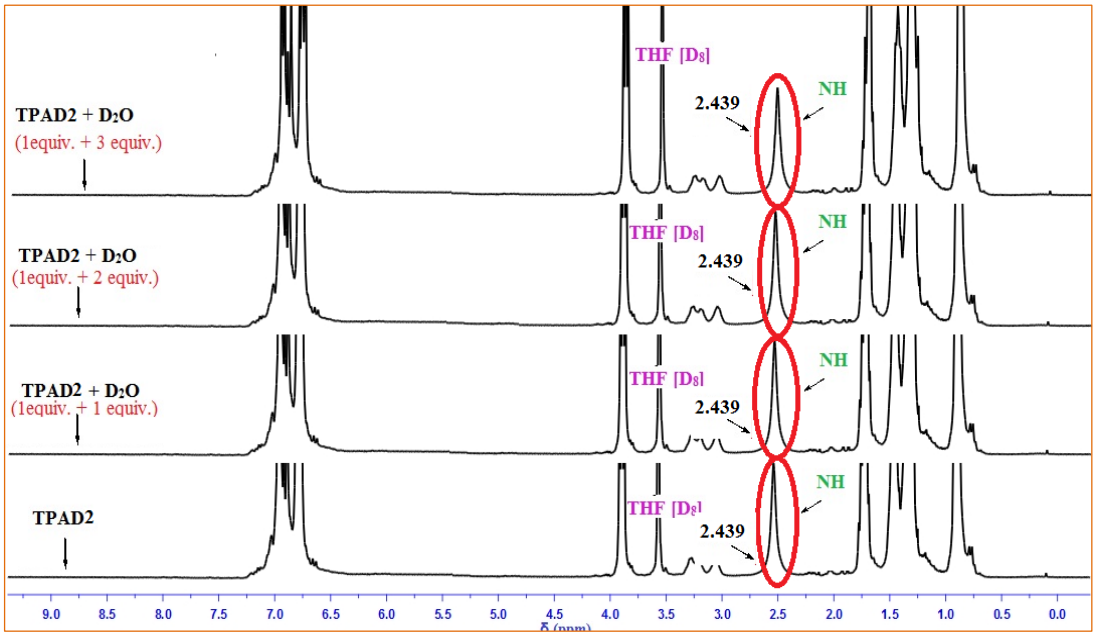

Fig. S26 ^{1}H NMR titrations of **TPAD2** in THF [D_8] with **D_2O**, at room temperature and the final solvent composition is 3:1 in vol.

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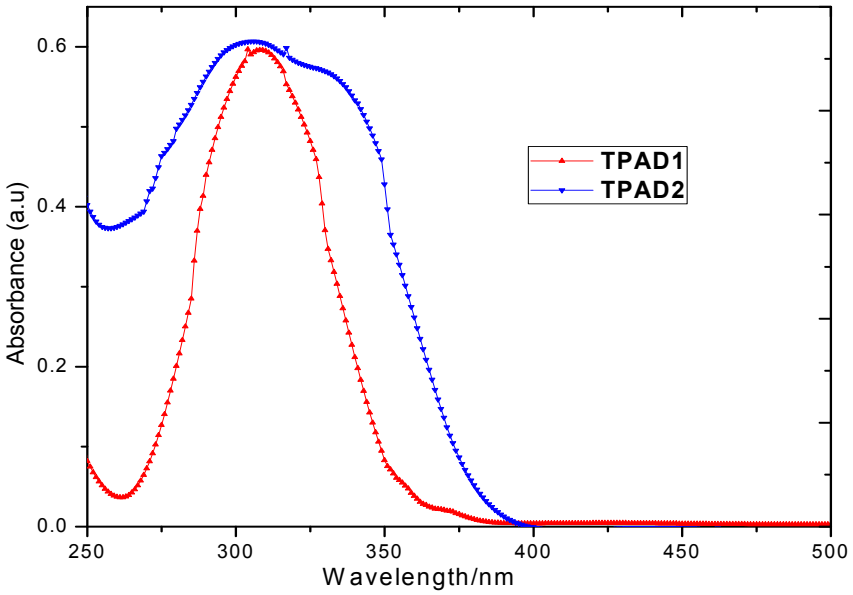

Fig. **S27** UV-Vis absorption spectra of **TPAD1** and **TPAD2** in THF (20 μM).

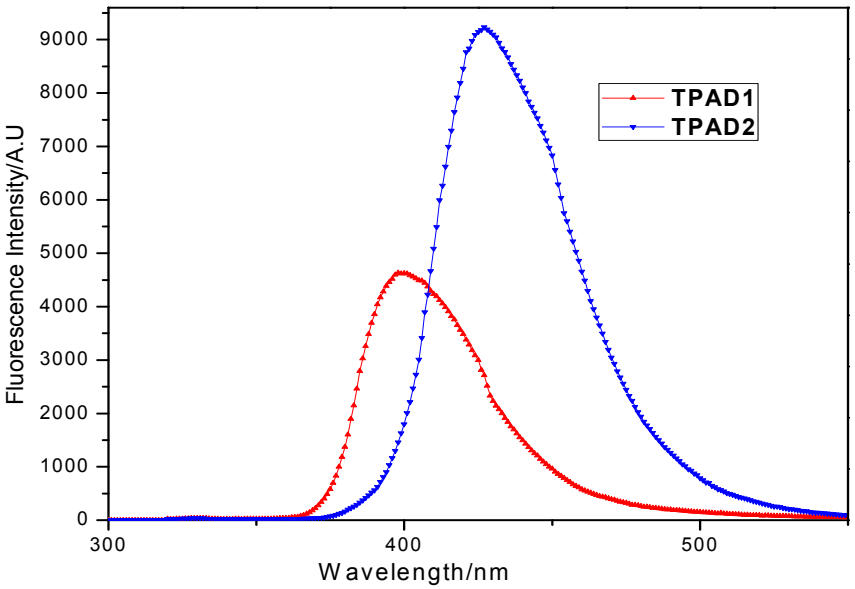

Fig. **S28** Fluorescence spectra of **TPAD1** and **TPAD2** in THF (20 μM).

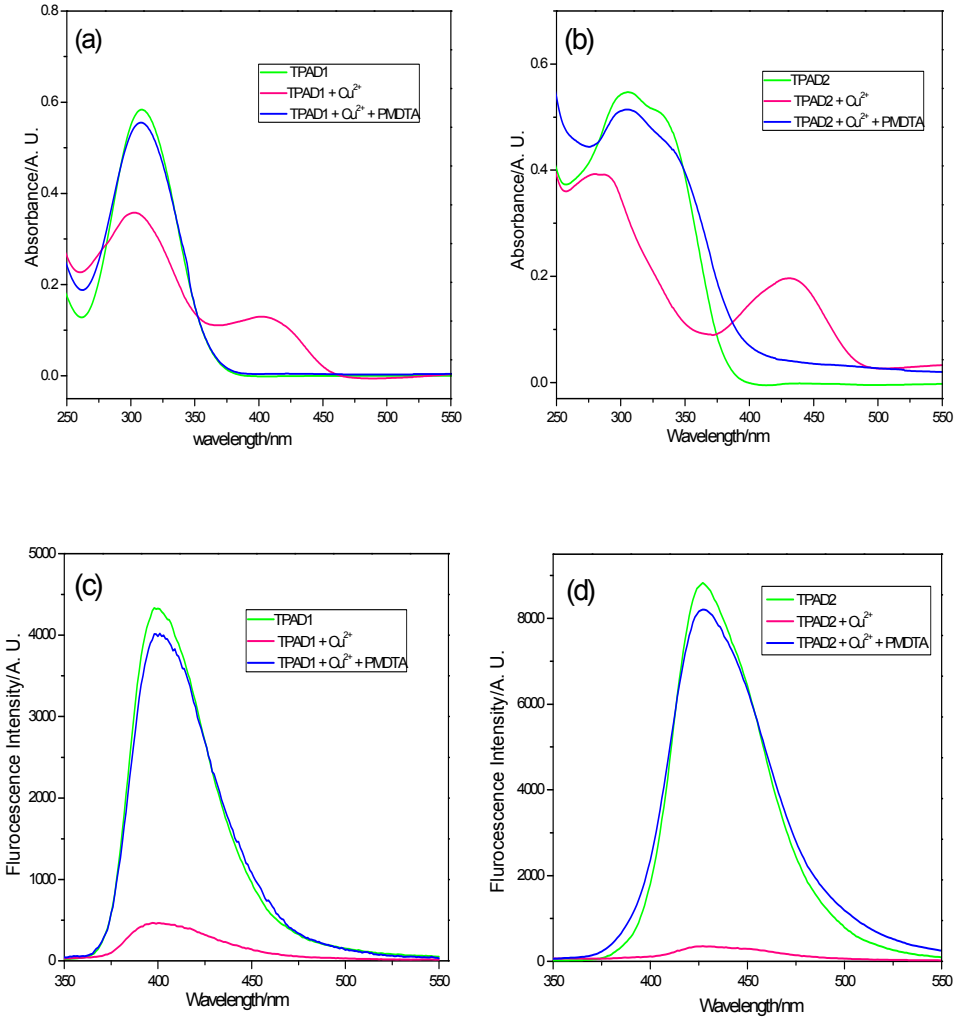

Fig. **S29** UV-Vis absorption spectra (a, b), fluorescence spectra (c, d) for sensor reversibilities of **TPAD1** and **TPAD2**, respectively.