Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Novel Carbazole-based Organogels Modulated by *Tert*-butyl Moieties

Xinchun Yang, Ran Lu,* Tinghua Xu, Pengchong Xue, Xingliang Liu and Yingying Zhao

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China

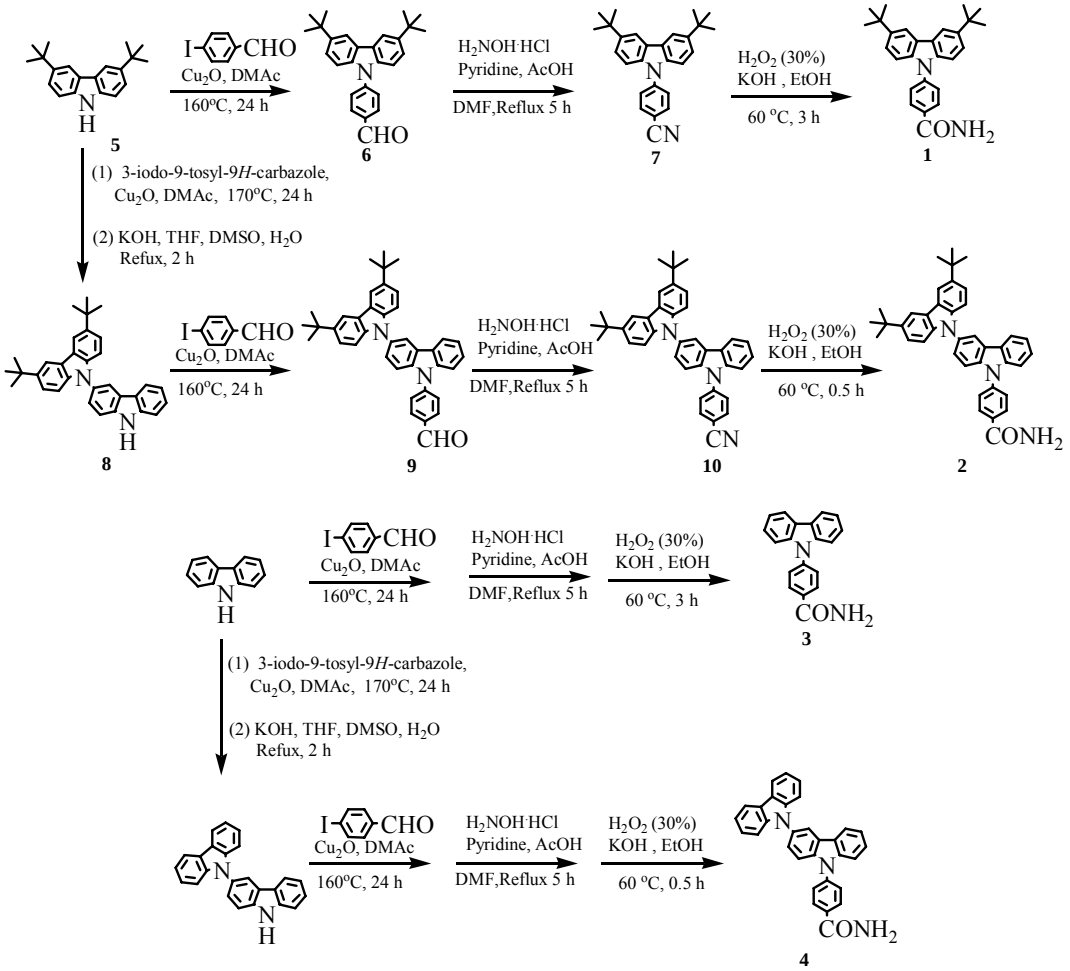
Fax: +86-431-88923907; E-Mail: luran@mail.jlu.edu.cn

1. General methods:

All solvents and reagents were purchased from commercial sources and used as received without further purification. The solvents for spectroscopic studies were of spectroscopic grade and used as received. ^{1}H NMR spectra were recorded on Mercury plus 500 MHz using $CDCl_3$ as solvent in all case. Mass spectra and HPLC (ELSD) data were recorded on an 1100 LC/MS system using a 4.6×50 mm column (5μm) with a linear gradient of 30-90 % (v/v) acetonitrile-water with 0.035% trifluoroacetic acid over 8 min with a flow rate of 3.5 mL/min. UV-vis absorption spectra were determined on a Shimadzu UV-1601PC Spectrophotometer. Fluorescence spectra were carried out on a Shimadzu RF-5301 Luminescence Spectrometer at room temperature. Fluorescence images were taken on Fluorescence Microscope (Olympus Reflected Fluorescence System BX51, Olympus, Japan). IR Spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating samples in KBr pellet. X-Ray diffraction (XRD) pattern was carried out on a Japan Rigaku D/max-γA instrument. XRD was equipped with graphite monochromatized Cu-Kα radiation (λ = 1.5418Å), employing a scanning rate of 0.02° s^{-1} in the 2θ range from 0.7° to 10°. Scanning electron microscopy (SEM) observations were carried out on a Japan Hitachi model X-650 San electron microscope. The samples for these measurements were prepared by casting the organogel on silicon wafers and dried at room temperature, and then were coated by gold. Transmission electron microscopy (TEM) was taken with a Hitacdhi moes H600A-2 apparatus by wiping the samples onto a

200-mesh copper grid followed by naturally evaporating the solvent. Atomic force microscopy (AFM) images were taken with a Nanoscope IIIa AFM Multimode (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si cantilevers. The fluorescence quantum yields were determined against quinine sulfate in 0.1 N H_2SO_4 (Φ_F = 0.546) as the standard.

2. Synthetic Procedures and Characterizations.



3,6-Di-tertbutyl-9H-carbazole (**5**), 4-(3,6-Di-tertbutyl-9H-carbazol-9-yl)benzaldehyde (**6**), and 3-iodo-9-tosyl-9H-carbazole were prepared according to the literatures.[1-3]

4-(3,6-di-tertbutyl-9H-carbazol-9-yl)benzonitrile (7):

A mixture of 4-(3,6-di-tertbutyl-9H-carbazol-9-yl)benzaldehyde **6** (1.0 g, 2.6 mmol), $H_2NOH{\cdot}HCl$ (0.35 g, 5.03 mmol), pyridine (0.58 g, 7.3 mmol), AcOH (0.87 g, 14 mmol), and DMF (10 mL) were stirred and refluxed for 5 h. After cooling to room temperature, the mixture was poured into 50 mL H_2O and stirred for 20 min. The solid was collected by filtration, and recrystallized from ethyl acetate / petroleum ether (1:10 v/v) to give 0.91 g (92 %) of a white solid, mp: 212.0-214.0 °C. IR (KBr, cm^{-1}): 3070, 2959, 2228, 1604, 1512. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ = 8.15 (2 H, s, Ar-H), 7.91 (2 H, d, Ar-H), 7.75 (2 H, d, Ar-H), 7.51 (2 H, d, Ar-H), 7.43 (2 H, d, Ar-H), 1.49 (18 H, s, $-CH_3$). MS, m/z: cal.: 380.5, found: 381.3 [M^+ + H].

4-(3,6-di-tertbutyl-9H-carbazol-9-yl)benzamide (1):

A mixture of 4-(3,6-di-tertbutyl-9H-carbazol-9-yl)benzonitrile **7** (0.8 g, 2.0 mmol), 30 % H_2O_2 (5.7 g, 50.0 mmol), KOH (1 g, 17.9 mmol), and EtOH (10 mL) were stirred for 3 h at 60 °C. After cooling to room temperature, the mixture was poured into 50 mL H_2O, neutralized by HCl and stirred for 20 min. The solid was collected by filtration, and recrystallized from cyclohexane / ethyl acetate (10:1 v/v) to give 0.5 g (62 %) of a white solid, mp: 166.0-168.0 °C. IR (KBr, cm^{-1}): 3346, 3184, 2960, 1662, 1604. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ = 8.14 (2 H, s, Ar-H), 8.05 (2 H, d, Ar-H), 7.68 (2 H, d, Ar-H), 7.48 (2 H, d, Ar-H), 7.39 (2 H, d, Ar-H), 6.16 (1 H, s, N-H), 5.83 (1 H, s, N-H), 1.48 (18 H, s, $-CH_3$) (Fig. S7 and S8). MS, m/z: cal.: 398.5, found: 399.2 [M^+ + H] and 797.4 [$2M^+$ + H] (Fig. S13).

3,6-di-tertbutyl-9-(9H-carbazol-3-yl)-9H-carbazole (8):

3,6-Di-tertbutyl-9H-carbazole (3.6 g, 12.0 mmol) **5**, 3-iodo-9-tosylcarbazole (5.5 g, 12.3 mmol), Cu_2O (3.0 g, 21.0 mmol), and DMAc (20 mL) were filled sequentially into a seal-tube under nitrogen atmosphere and heated to 160 °C in oil bath for 24 h. Then, the mixture was cooled to room temperature and filtrated. The filtrate was poured into 300 mL H_2O and stirred for 20 min. The solid was collected by filtration, and recrystallized from EtOH / THF (4:1 v/v) to give 4.4 g (62 %) of white solid. The obtained products (4.0 g, 6.7 mmol) were dissolved in mixed solvents containing THF (20 mL), DMSO (10 mL) and H_2O (3 mL), then KOH (5.0 g, 89 mmol) was added. The mixture was refluxed for 4 h, cooled to room temperature, neutralized by HCl, and then poured into water. The solid was collected by filtration, and recrystallized from EtOH to give 2.7 g (91 %) of white solid. mp: >250 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 11.54 (1 H, s, N-H), 8.34 (1 H, d, Ar-H), 8.30 (2 H, d, Ar-H), 8.20 (1 H, d, Ar-H), 7.72 (1 H, d, Ar-H), 7.52-7.57 (2 H, m, Ar-H), 7.42-7.48 (3 H, m, Ar-H), 7.25 (2 H, d, Ar-H), 7.17 (1 H, t, Ar-H), 1.43 (18 H, s, -CH_3). MS, m/z: cal.: 444.6, found: 445.2 [M^+ + H].

4-[3-(3,6-di-tertbutyl-9H-carbazol-9-yl)-9H-carbazol-9-yl]benzaldehyde (9):

3,6-Di-tertbutyl-9-(9H-carbazol-3-yl)-9H-carbazole **8** (1.5 g, 2.8 mmol), 4-iodobenzaldehyde (0.9 g, 3.9 mmol), Cu_2O (0.9 g, 6.3 mmol), and DMAc (5 mL) were filled sequentially in a seal-tube under nitrogen atmosphere and heated to 170 °C in oil bath for 20 h. Then, the mixture was cooled to room temperature and filtrated.

The filtrate was poured into 200 mL H_2O and stirred for 20 min. The solid was collected by filtration, and purified by chromatography (silica gel, petroleum ether / ethyl acetate = 20:1 v/v) to give 1.4 g of a light-yellow solid, which was further recrystallized from EtOH : THF (4:1 v/v) to give 1.2 g (75 %) of a light-yellow solid, mp: 210.0-212.0 °C. IR (KBr, cm^{-1}): 3062, 2962, 2865, 1703, 1600, 1512. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ = 10.16 (1 H, s, -CHO), 8.28 (1 H, s, Ar-H), 8.20 (4 H, d, Ar-H), 8.10 (1 H, d, Ar-H), 7.88 (2 H, d, Ar-H), 7.68 (1 H, d, Ar-H), 7.56 (2 H, t, Ar-H), 7.46-7.51 (3 H, m, Ar-H), 7.34 (3 H, t, Ar-H), 1.48 (18 H, s, $-CH_3$). MS, m/z: cal.: 548.7, found: 549.4 [M^+ + H].

4-[3-(3,6-di-tertbutyl-9H-carbazol-9-yl)-9H-carbazol-9-yl]benzonitrile (10):

A mixture of **9** (1.0g, 1.8 mmol), $H_2NOH{\cdot}HCl$ (0.18 g, 2.5 mmol), pyridine (0.29 g, 3.7 mmol), AcOH (0.44 g, 7 mmol), and DMF (5 mL) was stirred and refluxed for 8 h. After cooling to room temperature, the mixture was poured into 30 mL H_2O and stirred for 20 min. The solid was collected by filtration, and recrystallized from petroleum ether /ethyl acetate (10:1 v/v) to give 0.90 g (91 %) of a white solid, mp: 194.0-196.0 °C. IR (KBr, cm^{-1}): 3047, 2955, 2864, 2229, 1603, 1511. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ = 8.27 (1 H, s, Ar-H), 8.18 (2 H, s, Ar-H), 8.10 (1 H, d, Ar-H), 7.98 (2 H, d, Ar-H), 7.84 (2 H, d, Ar-H), 7.62 (1 H, d, Ar-H), 7.57 (1 H, t, Ar-H), 7.51 (2 H, s, Ar-H), 7.46 (2 H, d, Ar-H), 7.36 (1 H, s, Ar-H),7.32 (2 H, d, Ar-H), 1.48 (18 H, s, $-CH_3$). MS, m/z: cal.:545.7, found: 546.4 [M^+ + H].

4-[3-(3,6-di-tertbutyl-9H-carbazol-9-yl)-9H-carbazol-9-yl]benzamide (2):

A mixture of 4-(3-(3,6-di-tertbutyl-9H-carbazol-9-yl)-9H-carbazol-9-yl)benzonitrile **10** (0.8 g, 1.4 mmol), 30 % H_2O_2 (4.0 g, 35.0 mmol), KOH (0.7g, 12.6 mmol) , EtOH (10 mL), was stirred for 0.5 h at 60 °C. After cooling to room temperature, the mixture was poured into 20 mL H_2O, neutralized by HCl and stirred for 20 min. The solid was collected by filtration, and recrystallized from petroleum ether / ethyl acetate (10:1 v/v) to give 0.5 g (60 %) of a white solid, mp: 232.0-234.0 °C. IR (KBr, cm^{-1}): 3367, 3049, 2918, 1703, 1597, 1512 . ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ = 8.27 (1 H, s, Ar-H), 8.19 (2 H, s, Ar-H), 8.12 (3 H, d, Ar-H), 7.80 (2 H, d, Ar-H), 7.62 (1 H, d, Ar-H), 7.57 (1 H, d, Ar-H), 7.49 (4 H, d, Ar-H), 7.34 (3 H, s, Ar-H), 6.22 (1H, s, N-H), 5.88 (1H, s, N-H), 1.48 (18 H, s, $-CH_3$) (Fig. S9 and S10). MS, m/z: cal.: 563.7, found: 564.2 [M^+ + H] (Fig. S14).

4-(9H-carbazol-9-yl)benzamide (3):

By following the above synthetic procedures for **1**, compound **3** was obtained as a white solid, mp: 202.0-204.0 °C. IR (KBr, cm^{-1}): 3386, 3196, 1647, 1618, 1518. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ = 8.18 (2 H, d, Ar-H), 8.09 (2 H, d, Ar-H), 7.73 (2 H, d, Ar-H), 7.49-7.44 (4 H, m, Ar-H), 7.35 (2 H, t, Ar-H), 6.18 (1 H, s, N-H), 5.75 (1 H, s, N-H) (Fig. S11). MS, m/z: cal.: 286.3, found: 287.0 [M^+ + H] (Fig. S15).

4-[3-(9H-carbazol-9-yl)-9H-carbazol-9-yl]benzamide (4):

By following the above synthetic procedures for **2**, compound **4** was obtained as a

white solid, mp: 174.0-176.0 °C. IR (KBr, cm^{-1}): 3341, 3187, 1667, 1606, 1516. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ = 8.30 (1 H, s, Ar-H), 8.20 (2 H, d, Ar-H), 8.12 (3 H, d, Ar-H), 7.79 (2 H, d, Ar-H), 7.64 (1 H, d, Ar-H), 7.57 (1 H, d, Ar-H), 7.51 (2 H, s, Ar-H), 7.41 (4 H, d, Ar-H), 7.36 (1 H, d, Ar-H), 7.31 (2 H, t, Ar-H), 6.18 (1 H, s, N-H), 5.71 (1 H, s, N-H) (Fig. S12). MS, m/z: cal.: 451.5, found: 452.0 [M^+ + H] (Fig. S16).

3. Gelation test of compounds 1-4 in various organic solvents.

The weighted compounds **1-4** in solvents were heated in sealed test tubes in an oil bath until the solid were dissolved respectively. After the solution was allowed to stand at room temperature for a certain time (from 2 min to 5 h), the state of the mixture was evaluated by the "stable to inversion of a test tube" method.

Reference:

1. F. A. Neugebauer, H. Fisher, *Chem. Ber.* 1972, **105**, 2686.
2. A. Kimoto, J. S. Cho, M. Higuchi, K. Yamamoto, *Macromolecules* 2004, **37**, 5531. F. Loiseau, S. Campagna, A. Hameurlaine, W. Dehaen, *J. Am. Chem. Soc.* 2005, **127**, 11352.
3. S. H.Tucker, *J. Chem. Soc.* 1926, 546.

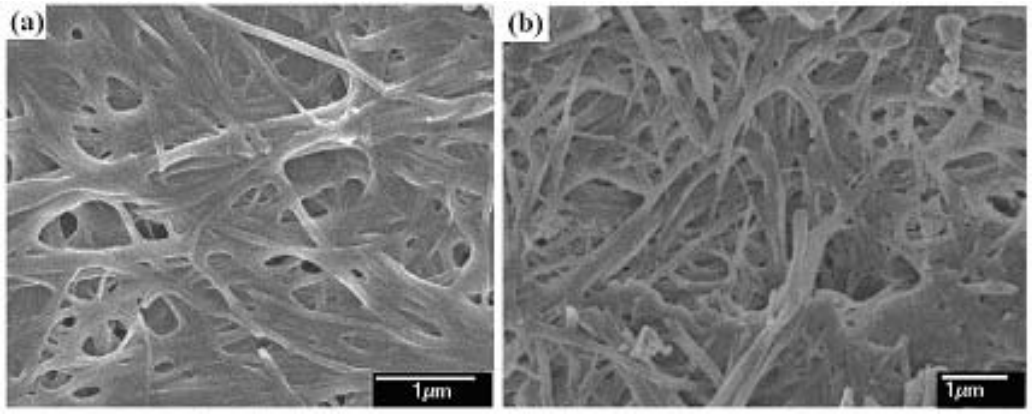


Fig. S1 SEM images of the dried gels of **1** (a) and **2** (b) obtained from cyclohexane (0.2 wt %).

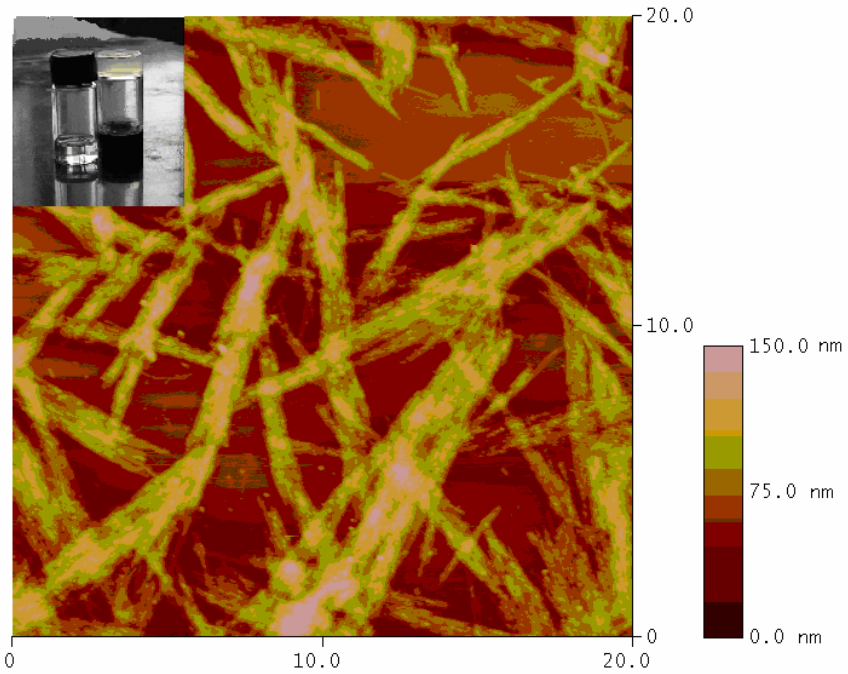


Fig. S2 AFM height image (20 × 20 μm^2) of a dried gel of **2** obtained from cyclohexane (0.2 wt %). The inset photos are cyclohexane solution of **2** at 70 °C (left vial) and cyclohexane gel **2** at 25 °C (right vial) at 0.2 wt %.

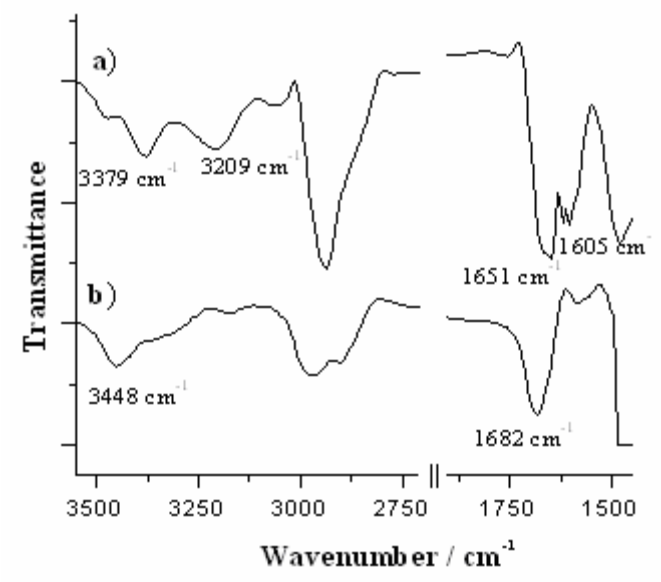


Fig. S3 FT-IR spectra of **1** in a dried gel obtained from cyclohexane (0.2 wt %) (a) and in THF solution (b).

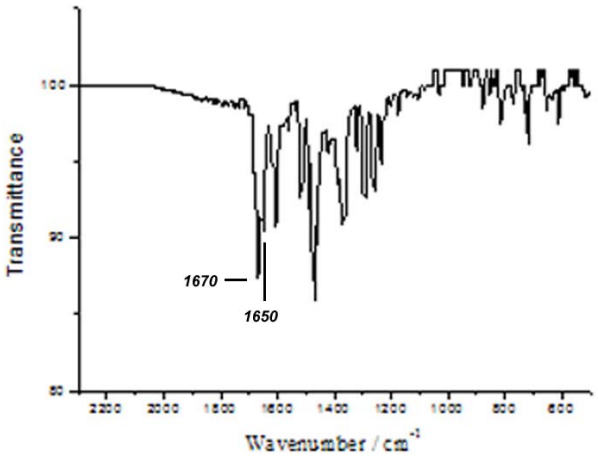


Fig. S4 FT-IR spectrum of **1** in a destroyed gel system by addition of a drop of methanol.

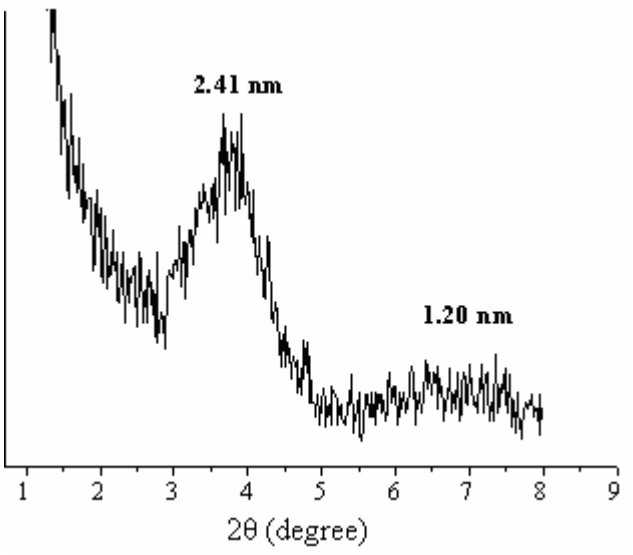


Fig. S5 XRD diffraction of a dried gel **1** obtained from cyclohexane (0.2 wt %).

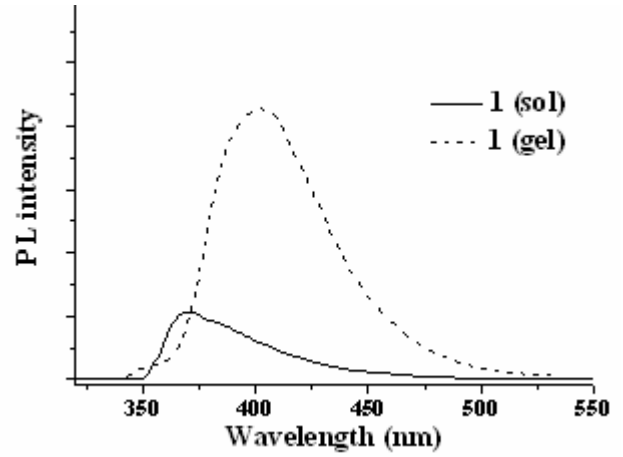


Fig. S6 PL emission spectra of **1** in cyclohexane (4×10^{-3} M) at 70 °C and the corresponding gel (0.2 wt %) obtained in cyclohexane excited at 297 nm.

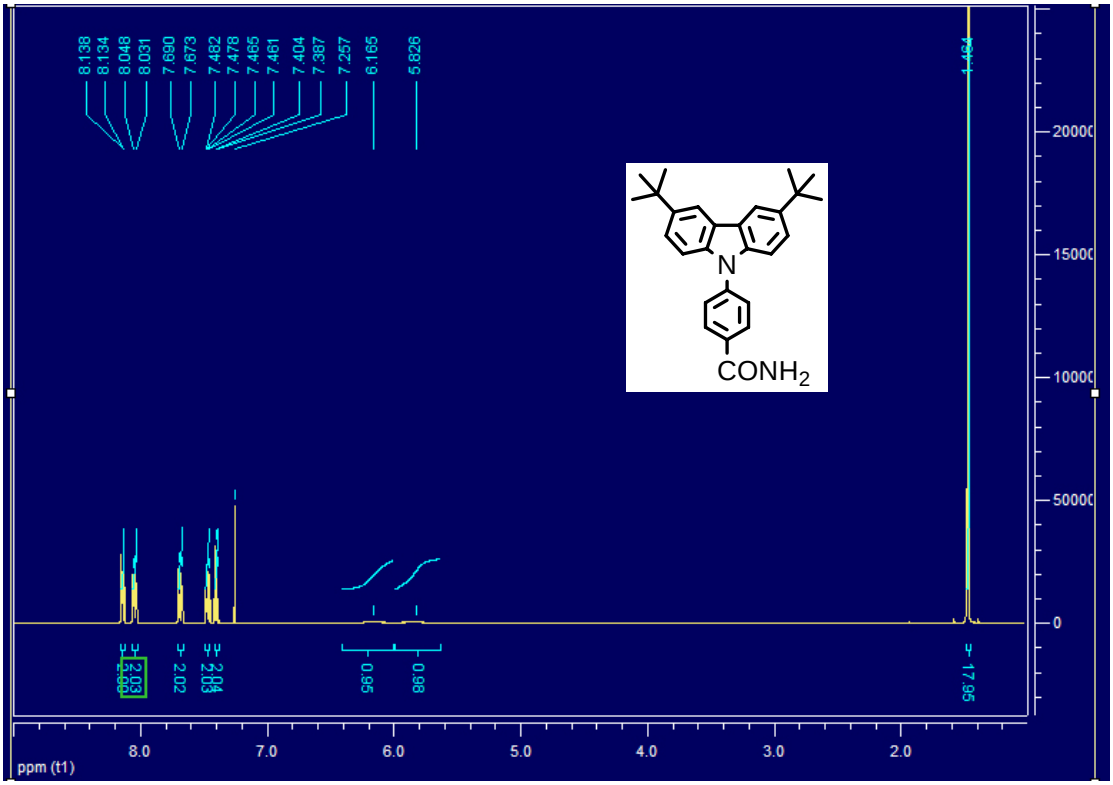


Fig. S7 ^{1}H NMR (500 MHz) spectrum of compound **1**.

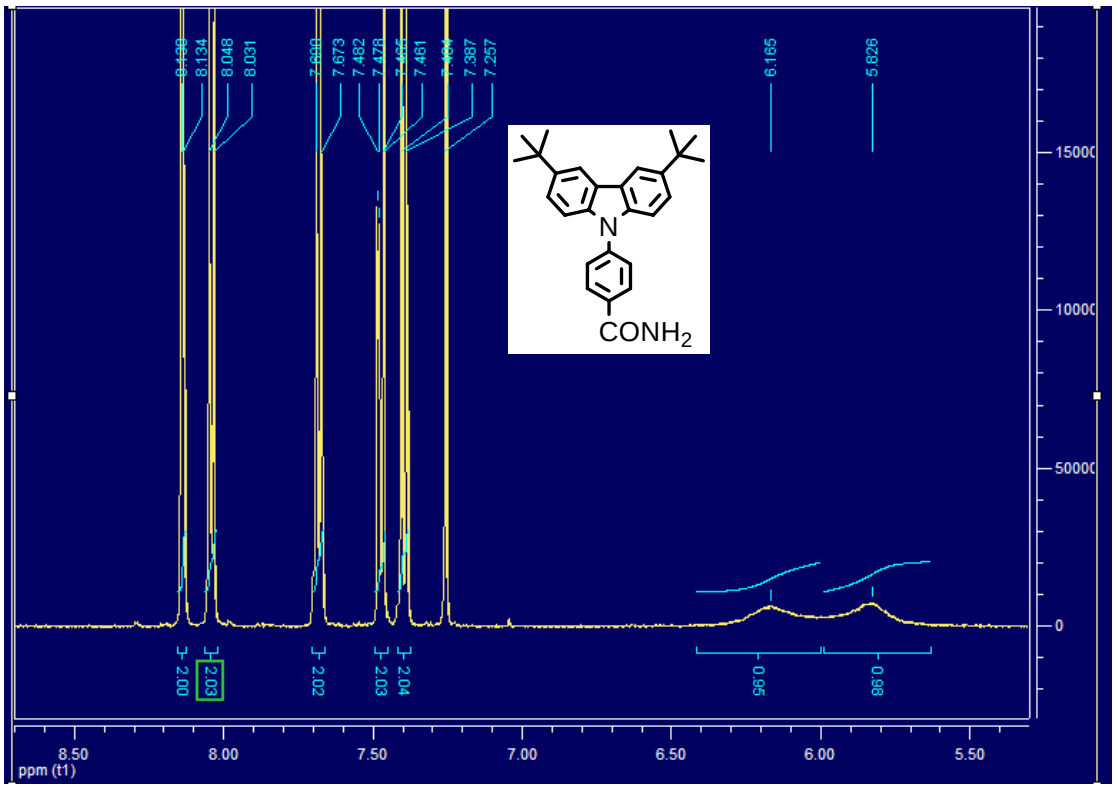


Fig. S8 ^{1}H NMR (500 MHz) spectrum of compound **1**.

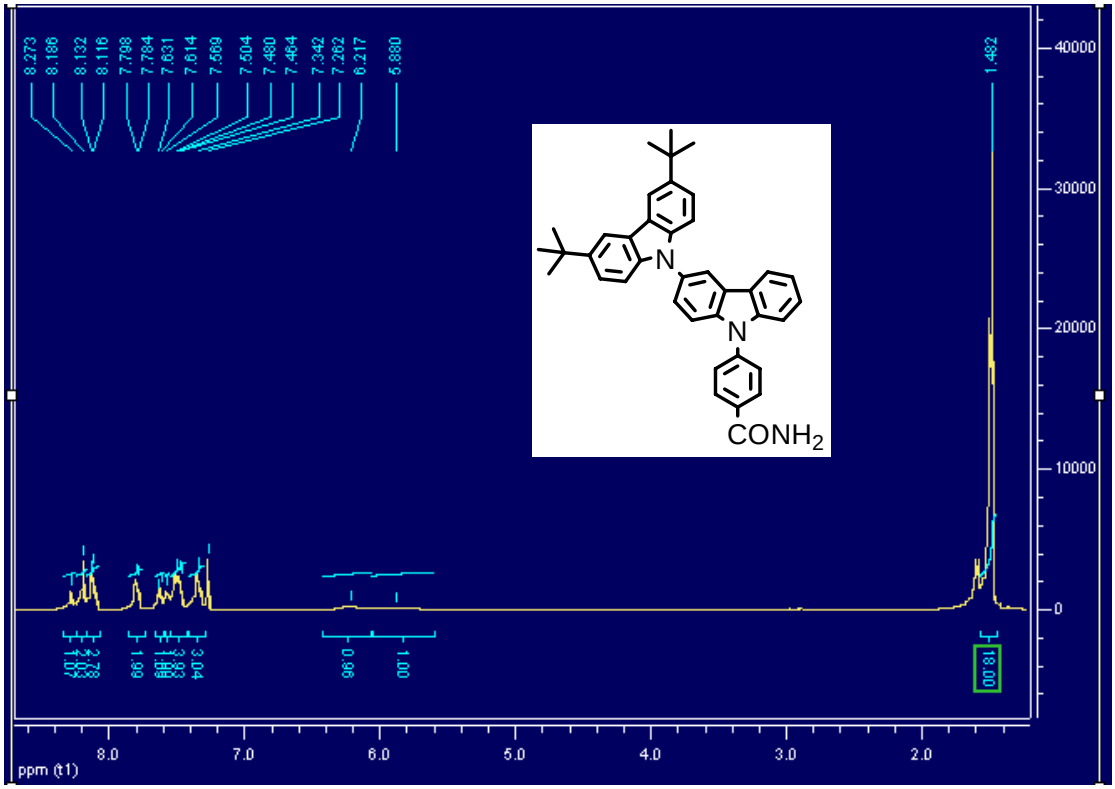


Fig. S9 ^{1}H NMR (500 MHz) spectrum of compound **2**.

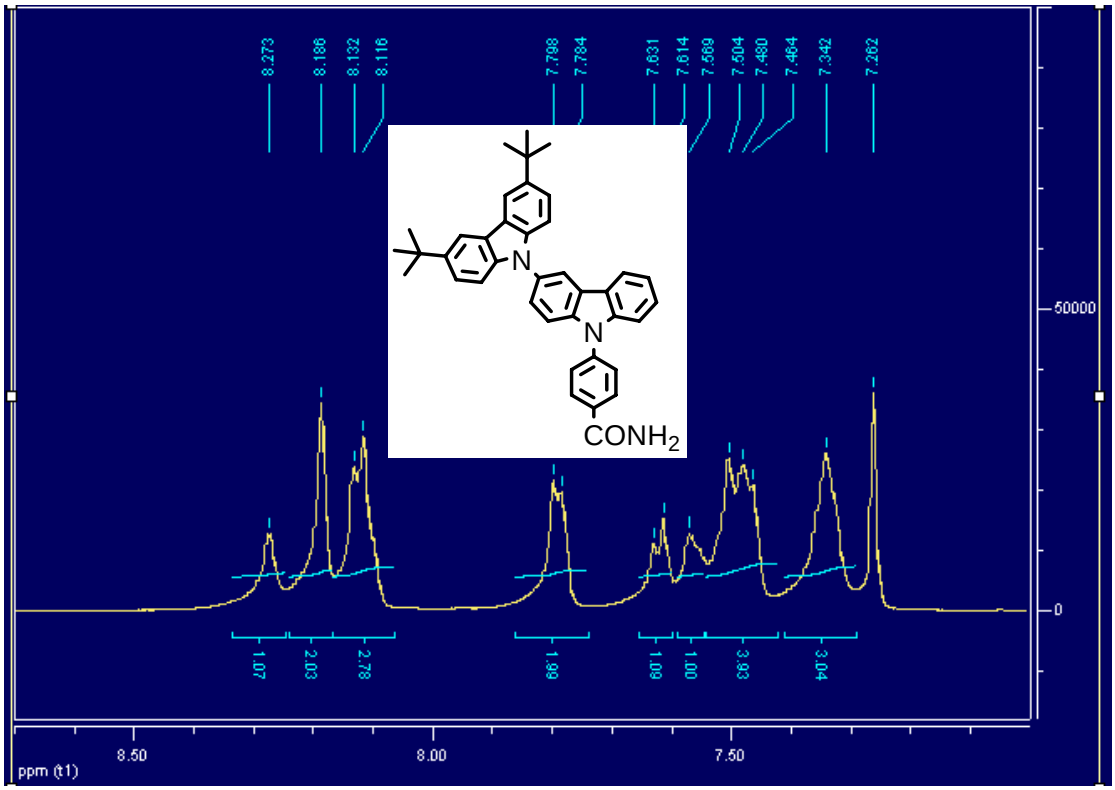


Fig. S10 ^{1}H NMR (500 MHz) spectrum of compound **2**.

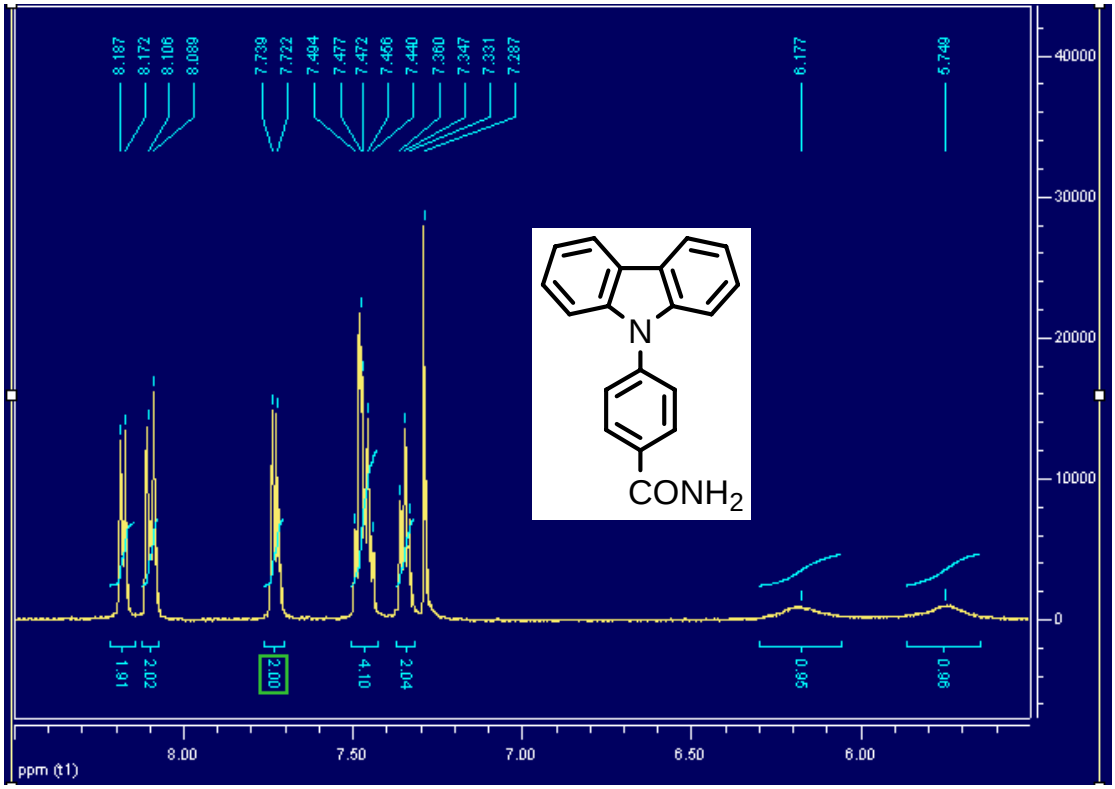


Fig. S11 ^{1}H NMR (500 MHz) spectrum of compound **3**.

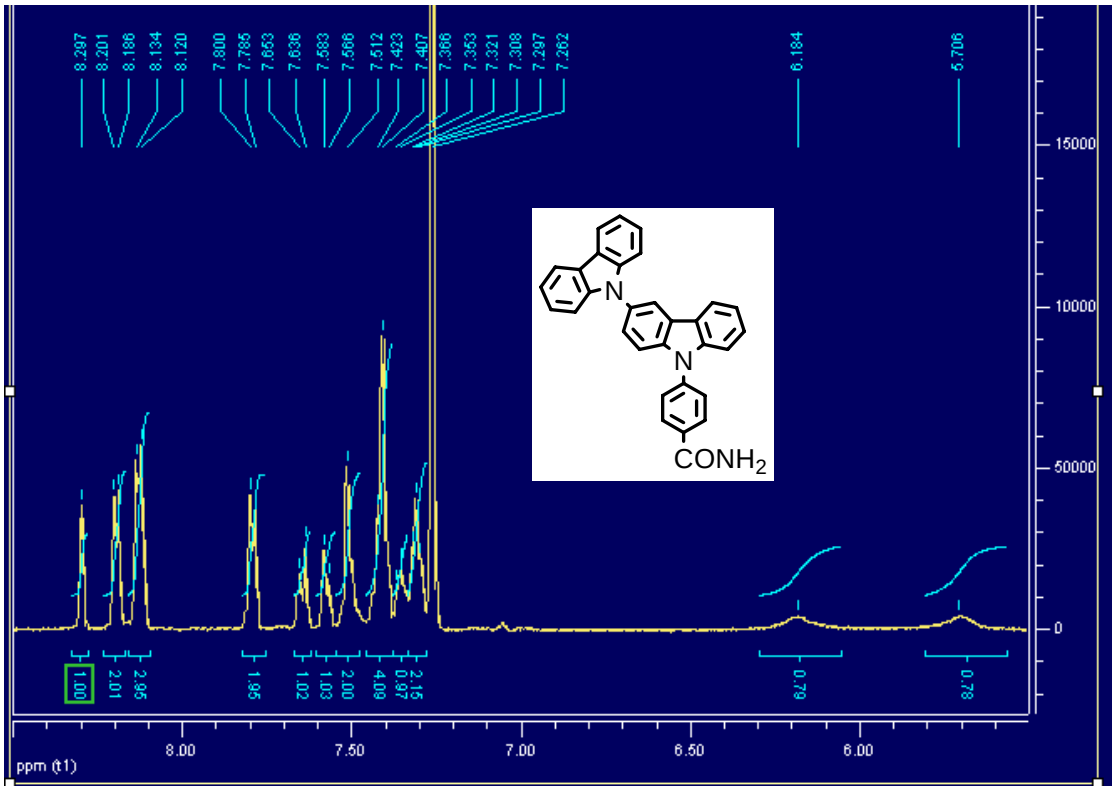


Fig. S12 ^{1}H NMR (500 MHz) spectrum of compound **4**.

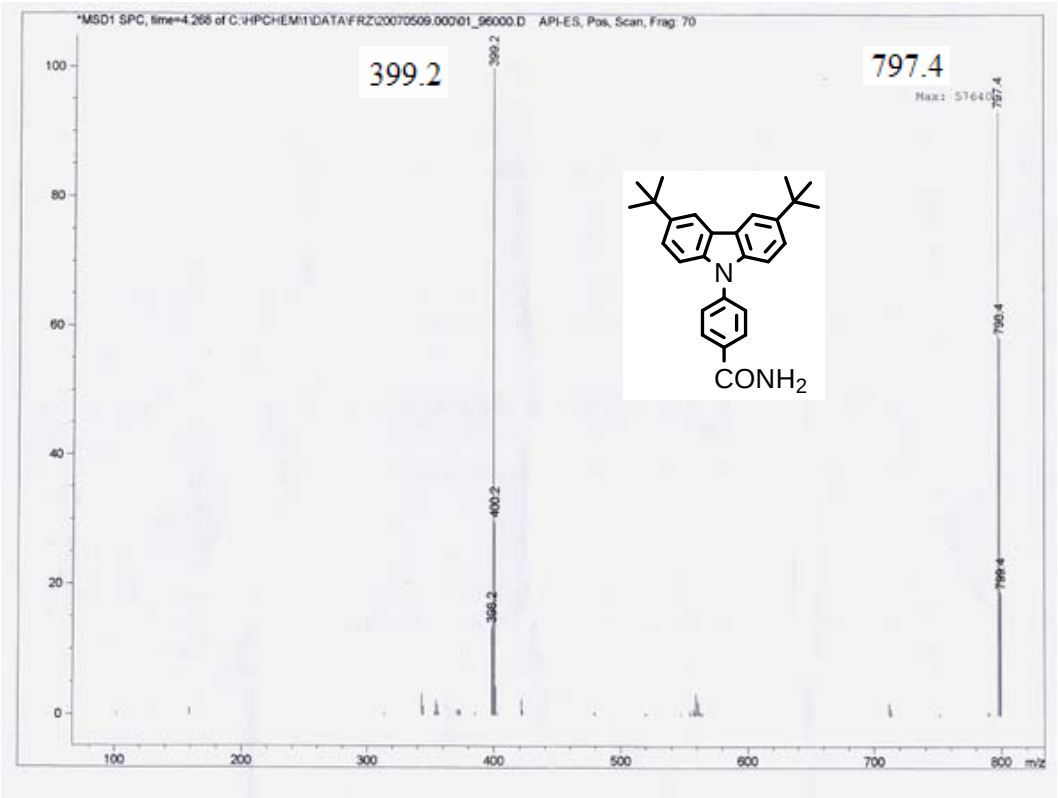


Fig. S13 MS spectrum of compound **1**.

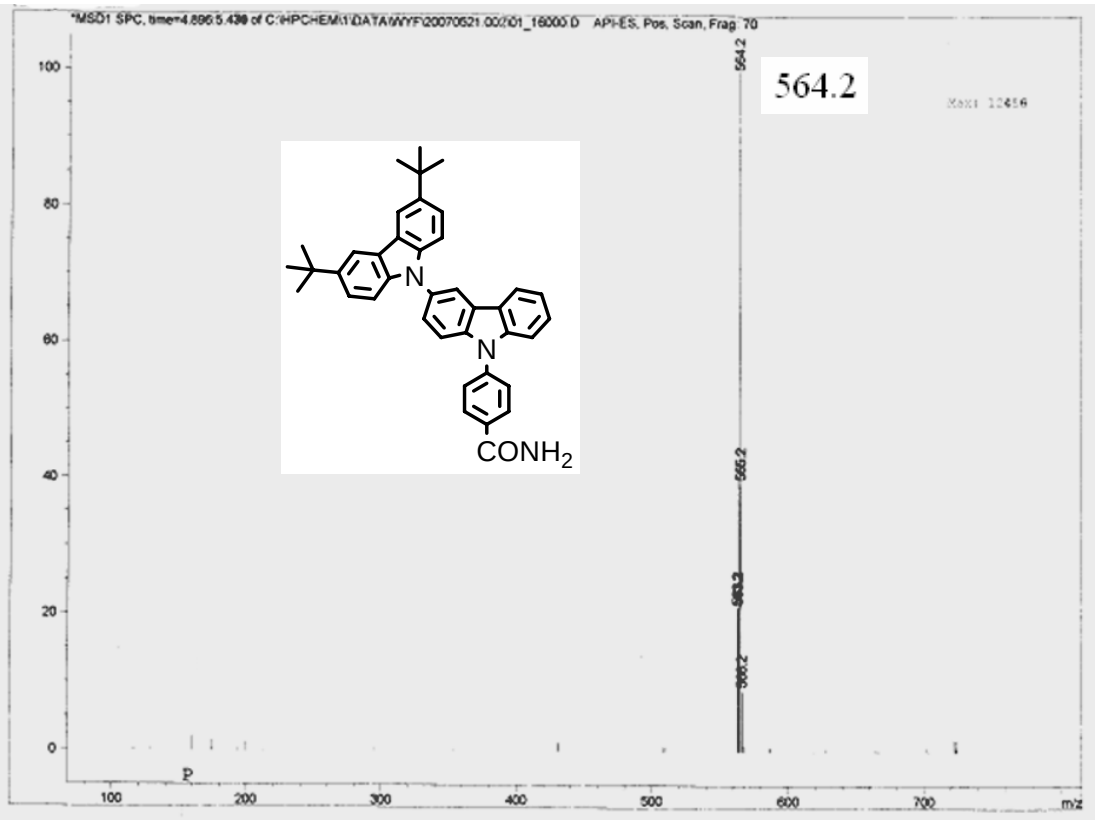


Fig. S14 MS spectrum of compound **2**.

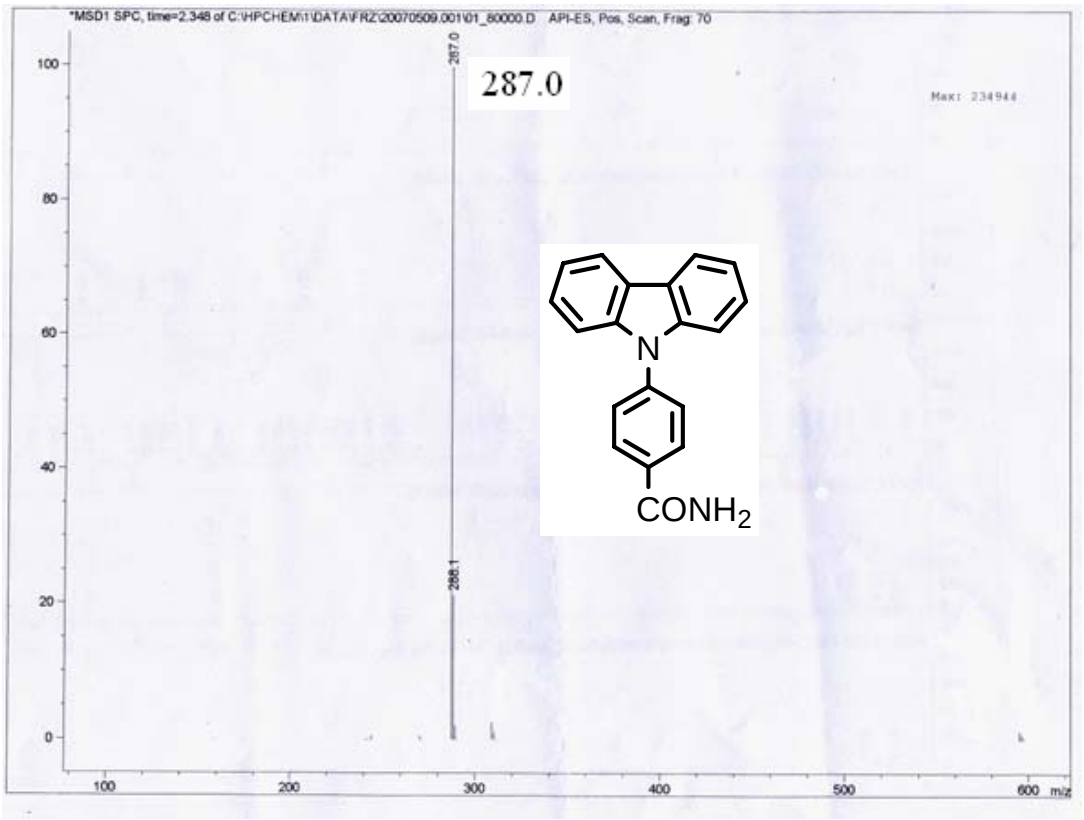


Fig. S15 MS spectrum of compound **3**.

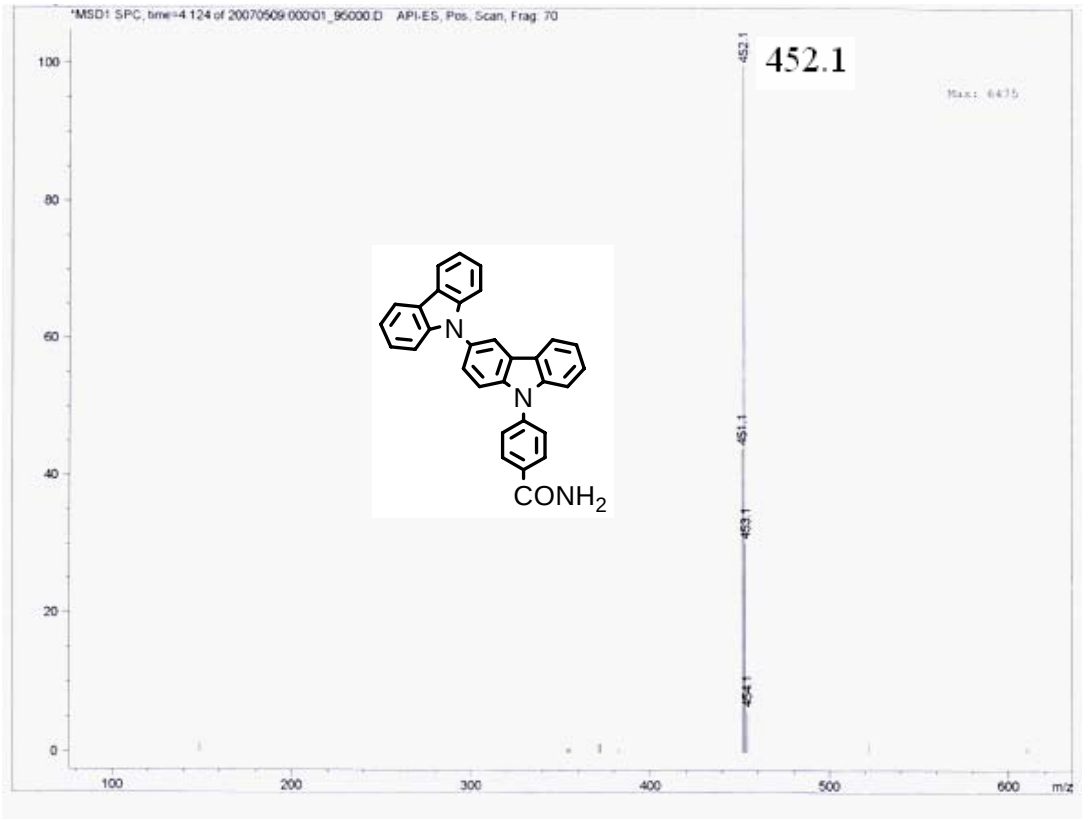


Fig. S16 MS spectrum of compound **4**.