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Liquid-crystalline TADF materials based on Substituted Carbazoles and Terephthalonitrile

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Supplementary Information

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General information

NMR spectra were recorded on a JEOL ECX spectrometer at 298 K. ^{1}H NMR (400 MHz) chemical shifts are referenced to residual $CHCl_3$ (δ 7.26) in $CDCl_3$, DCM (δ 5.32) in methylene chloride-d_2 and DMSO in DMSO-d_6. ^{13}C NMR (100 MHz) chemical shifts are reported relative to $CDCl_3$ (δ 77.3), DCM-d_2 (δ 54.00) and DMSO-d_6 (δ 39.52). ^{11}B NMR (128 MHz) and ^{19}F NMR (376 MHz) chemical shifts are uncorrected. Elemental analysis was carried out on an Exeter Analytical Inc. CE-440 analyser. Accurate mass measurement analyses were conducted using matrix-assisted laser desorption/ionization (MALDI). Optical textures were recorded using an Olympus BX50 polarising microscope equipped with a Linkam scientific LTS350 heating stage, Linkam LNP2 cooling pump and Linkam TMS92 controller. DSC was performed on a Mettler DSC822e fitted with an autosampler operating with Mettler Star-E software and calibrated before use against an indium standard (onset = 156.55 ± 0.2°C, ΔH = 28.45 ± 0.40 J g^{-1}), with all runs performed under an atmosphere of dry nitrogen.

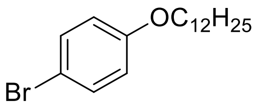
All reagents were purchased from commercial sources and used as received. Solvents were purified with drying cartridges through a solvent delivery system. Reactions were monitored by TLC using silica gel (F_{254} plates, 60 Å porosity). TLC analysis was visualized using UV light. The products were purified by chromatography on silica gel (60 Å porosity, 35-75 µm) or aluminium oxide (60 Å porosity, 50-200 µm, neutral).

The UV-Vis absorption spectra were measured with a Varian Cary 300 double beam spectrometer. The emission and excitation spectra were measured with a Horiba Jobin Yvon Fluorolog-3 steady-state fluorescence spectrometer. The emission decay times were measured with a PicoBright PB-375 pulsed diode laser (λ_{exc} = 378 nm, pulse width 100 ps) used as the excitation source, and the PL signal was detected with a cooled photomultiplier attached to a FAST ComTec multichannel scalar PCI card with a time resolution of 250 ps. The PL quantum yield was determined with a Hamamatsu C9920-02 system equipped with a Spectralon® integrating sphere.

All calculations were carried out with the Gaussian 09 package[1] utilising the DFT approach with the M11L functional[2] and the def2-SVP basis set[3]. Geometry optimisations were conducted with 'tight' criteria.

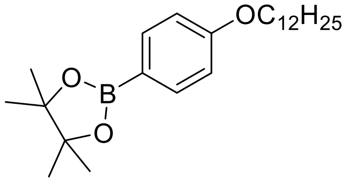
Synthetic procedures

4-Dodecyloxybromobenzene



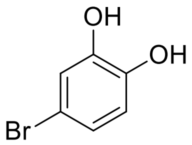
4-Bromophenol (10 g, 57.8 mmol) was dissolved in dry dimethylformamide (200 mL) and degassed by flushing nitrogen through the solution for 30 min. Potassium carbonate (16 g, 115.6 mmol) was added and the suspension was stirred for another 30 min at room temperature under a nitrogen atmosphere. After addition of 1-bromododecane (23.6 mL, 98.26 mmol), the reaction mixture was stirred at 80 °C overnight. After cooling to room temperature, the reaction mixture was poured into water (500 mL), and then extracted with hexane (2×200 mL). The combined organic layers were washed with water, and dried over anhydrous $MgSO_4$. Solvents were evaporated. Yield: 95% (18.88 g). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.35 (2H, d, *J* = 8.8 Hz, Ph), 6.76 (2H, d, *J* = 8.8 Hz, Ph), 3.90 (2H, t, *J* = 6.7 Hz, OCH_2), 1.76 (2H, m, CH_2), 1.43 (2H, m, CH_2), 1.26 (16H, m, alkyl), 0.88 (3H, t, *J* = 6.7 Hz, CH_3).

2-(4-Dodecyloxyphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane



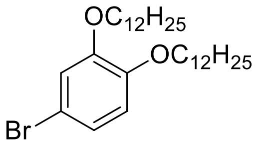
A flask charged with palladium catalyst Pd(dppf)Cl_2 (300 mg, 0.4 mmol), potassium acetate (6.1 g, 62.4 mmol), and bis(pinacolato)diboron (5.8 g, 23 mmol) was flushed with nitrogen. Anhydrous dimethyl sulfoxide (30 mL) and 4-dodecyloxybromobenzene (7.1 g, 20.8 mmol) were then added. After being stirred at 90 °C overnight under a nitrogen atmosphere, the mixture was extracted with toluene (2×100 mL), washed with water and dried over anhydrous $MgSO_4$. The product was purified by column chromatography (silica gel, dichloromethane/petroleum ether (from 1/1 to 1/0)). Yield: 52% (4.2 g). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.73 (2H, d, *J* = 8.7 Hz, Ph), 6.88 (2H, d, *J* = 8.7 Hz, Ph), 3.97 (2H, t, *J* = 6.6 Hz, OCH_2), 1.77 (2H, m, CH_2), 1.44 (2H, m, CH_2), 1.33 (12H, s, CH_3), 1.26 (16H, m, CH_2), 0.88 (3H, t, *J* = 6.8 Hz, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 29.85.

3,4-Dihydroxybromobenzene



3,4-Dimethoxybromobenzene (5 mL, 39.2 mmol) was dissolved in dry dichloromethane (200 mL). Nitrogen was bubbled for 30 min to remove the oxygen. After cooling down to -78 °C for 30 min in dry ice/acetone bath, BBr_3 (1 M solution in heptane, 102 mL, 102 mmol) was added dropwise and the suspension was stirred at -78 °C for 30 min. Then the mixture was slowly warmed to 40 °C and stirred overnight. Saturated NH_4Cl aqueous solution was added dropwise at 0°C to quench the reaction. The mixture was extracted with ethyl acetate (2×150 mL). The organic phase was collected, dried over anhydrous $MgSO_4$ and evaporated. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate, 2/1). Yield: 98% (7.2 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (1H, d, J = 2.3 Hz, Ph), 6.91 (1H, dd, J = 8.6, 2.3 Hz, Ph), 6.74 (1H, d, J = 8.6 Hz, Ph), 6.00 (1H, s, OH), 5.79 (1H, s, OH).

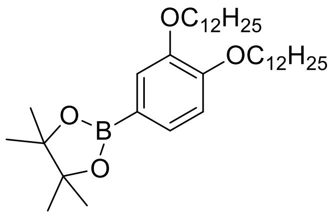
3,4-Didodecyloxybromobenzene



3,4-Dihydroxybromobenzene (3.1 g, 16.4 mmol) was dissolved in dry dimethylformamide (60 mL) and degassed by flushing nitrogen through the solution for 30 min. Potassium carbonate (9 g, 65.6 mmol) was added and the suspension was stirred for another 30 min at room temperature under a nitrogen atmosphere. After addition of 1-bromododecane (12.6 ml, 52.5 mmol), the reaction mixture was stirred overnight at 80 °C. After cooling to room temperature, the reaction mixture was poured into water (500 mL), and then extracted with hexane (3×100 mL). The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After evaporation of solvents, the product was purified by column chromatography (silica gel, hexane/ethyl acetate, 4/1), and dried under vacuum to give a product as a white solid. Yield: 96% (8.3 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (2H, m, Ph), 6.73 (1H, d, J = 9.1 Hz, Ph), 3.95 (4H, m, OCH_2), 1.80 (4H, m, CH_2), 1.44 (4H, m, CH_2), 1.26 (32H, m, alkyl), 0.88 (6H, t, J = 6.8 Hz, CH_3).

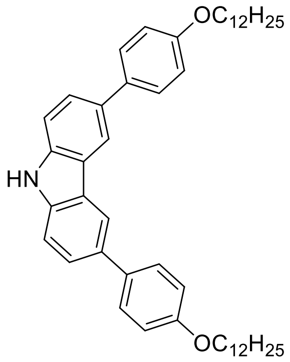
2-(3,4-Didodecyloxyphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane

A flask charged with palladium catalyst Pd(dppf)Cl_2 (155 mg, 0.2 mmol), potassium acetate (3.1 g, 32 mmol), and bis(pinacolato)diboron (3 g, 11.8 mmol) was flushed with nitrogen. Anhydrous dimethyl sulfoxide (50 mL) and 3,4-didodecyloxybromobenzene (5.6 g, 10.6 mmol) were then added. After being stirred at 90 °C overnight under a nitrogen atmosphere, the mixture was extracted with toluene (2×100 mL), washed with water and dried over anhydrous $MgSO_4$. The



product was purified by column chromatography (silica gel, dichloromethane/petroleum ether, 1/1). Yield: 61% (3.7 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (1H, dd, J =7.8, 1.6 Hz, Ph), 7.29 (1H, d, J = 1.6 Hz, Ph), 6.87 (1H, d, J = 7.8 Hz, Ph), 4.02 (4H, m, OCH_2), 1.81 (4H, m, CH_2), 1.46 (4H, m, CH_2), 1.33 (12H, s, CH_3), 1.26 (32H, m, alkyl), 0.88 (6H, t, J = 6.8 Hz, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.12.

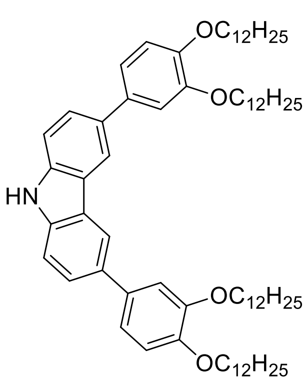
3,6-Di-(4-dodecyloxyphenyl)-9H-carbazole



A solution of 3,6-dibromocarbazole (1.4 g, 4.3 mmol) and 2-(4-dodecyloxyphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxa-borolane (4.2 g, 10.8 mmol) in a mixture of toluene (40 mL), ethanol (20 mL) and K_2CO_3 (5.95 g, 43 mmol) solution in water (10 mL) was degassed by argon bubbling for 30 min. $Pd(OAc)_2$ (0.19 g, 0.86 mmol) and S-Phos (0.7 g, 1.7 mmol) were added and the mixture was immediately transferred to a pre-heated oil bath and refluxed overnight. After hydrolysis (30 mL of water), the mixture was extracted with ethyl acetate (2 × 50 mL), washed with brine (50 mL), dried over $MgSO_4$, then filtered. The solvents were removed under reduced pressure and the crude material was purified by flash chromatography (deactivated alumina, petroleum ether/ethyl acetate, 5/1). Yield: 39% (1.16 g). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.29 (2H, d, J = 1.8 Hz, Cz), 8.24 (1H, broad, NH), 7.65 (2H, dd, J = 8.4, 1.8 Hz, Cz), 7.64 (4H, d, J = 8.8 Hz, Ph), 7.51 (2H, d, J = 8.4 Hz, Cz), 7.0 (4H, d, J = 8.8 Hz, Ph), 4.02 (4H, t, J = 6.6 Hz, OCH_2),1.81 (4H, m, CH_2), 1.49 (4H, m, CH_2), 1.28 (32H, m, alkyl), 0.89 (6H, t, J = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 158.9, 139.7, 134.8, 133.2, 128.6, 125.7, 124.4, 118.7, 115.3, 111.5, 38.7, 32.5, 30.2, 30.2, 30.2, 30.0, 29.9, 29.9, 26.6, 23.3, 14.5.

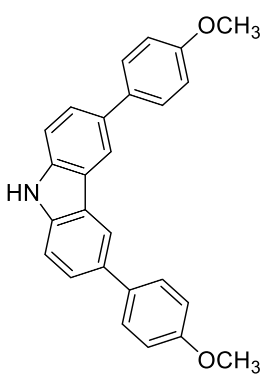
3,6-Di-(3,4-didodecyloxyphenyl)-9H-carbazole

A solution of 3,6-dibromocarbazole (0.84 g, 2.6 mmol) and 2-(3,4-didodecyloxyphenyl)-4,4,5,5-tetramethyl[1,3,2]-dioxaborolane (3.7 g, 6.4 mmol) in a mixture of toluene (20 mL), ethanol (10 mL) and K_2CO_3 (3.57 g, 26 mmol) solution in water (5 mL) was degassed by argon bubbling for 30 min. $Pd(OAc)_2$ (90 mg, 0.4 mmol) and S-Phos (325 mg, 0.8 mmol) were added and the mixture was immediately transferred to a pre-heated oil bath and refluxed for 48 h. After hydrolysis (150 mL of water), the mixture was extracted with ethyl acetate (2 × 200 mL), washed with brine (200 mL), dried over $MgSO_4$, then filtered. The solvents were removed under reduced pressure and the crude



material was purified by recrystallisation from ethanol. Yield: 55% (1.5 g). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.30 (2H, d, J = 1.8 Hz, Cz), 8.27 (1H, broad, NH), 7.66 (2H, dd, J = 8.4, 1.8 Hz, Cz), 7.51 (2H, d, J = 8.4 Hz, Cz), 7.26 (2H, d, J = 2.2 Hz, Ph), 7.23 (2H, dd, J = 8.3, 2.2 Hz, Ph), 6.99 (2H, d, J = 8.3 Hz, Ph), 4.10 (4H, t, J = 6.6 Hz, OCH_2), 4.03 (4H, t, J = 6.6 Hz, OCH_2), 1.83 (8H, m, CH_2), 1.50 (8H, m, CH_2), 1.28 (64H, m, alkyl), 0.88 (6H, t, J = 6.8 Hz, CH_3), 0.87 (6H, t, J = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 150.0, 148.9, 139.8, 135.6, 133.4, 125.8, 124.4, 120.0, 118.8, 114.9, 113.8, 111.5, 70.0, 70.0, 32.5, 30.3, 30.2, 30.0, 30.0, 29.9, 26.7, 23.3, 14.4.

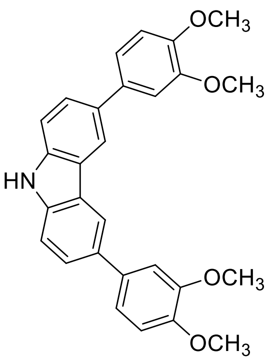
3,6-Di-(4-methoxyphenyl)-9H-carbazole



A solution of 3,6-dibromocarbazole (2 g, 6.15 mmol), 4-methoxyphenylboronic acid (2.3 g, 15.4 mmol) and K_2CO_3 (8.5 g, 61.5 mmol) in a mixture of toluene (40 mL), ethanol (20 mL) and water (10 mL) was degassed by nitrogen bubbling for 30 min. $Pd(OAc)_2$ (140 mg, 0.62 mmol) and S-Phos (504 mg, 1.23 mmol) was added and the mixture was refluxed overnight. After hydrolysis with water (30 mL), the mixture was extracted with ethyl acetate (2 × 50 mL), washed with brine (50 mL), dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure and the crude material was recrystallized from methanol and washed with cold methanol. Yield: 82% (1.9 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (2H, d, J = 1.8 Hz, Cz), 8.06 (1H, broad, NH), 7.65 (4H, d, J = 8.8 Hz, Ph), 7.64 (2H, dd, J = 8.4, 1.8 Hz, Cz), 7.46 (2H, d, J = 8.4 Hz, Cz), 7.03 (4H, d, J = 8.8 Hz, Ph), 3.88 (6H, s, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 139.2, 134.8, 132.9, 128.4, 125.4, 124.1, 118.5, 114.4, 111.0, 55.5.

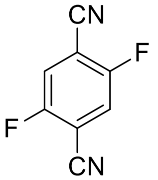
3,6-Di-(3,4-dimethoxyphenyl)-9H-carbazole

A solution of 3,6-dibromocarbazole (2 g, 6.15 mmol), 3,4-methoxyphenylboronic acid (1.4 g, 7.7 mmol) and K_2CO_3 (8.5 g, 61.5 mmol) in a mixture of toluene (40 mL), ethanol (20 mL) and water (10 mL) was degassed by nitrogen bubbling for 30 min. $Pd(OAc)_2$ (207 mg, 0.92 mmol) and S-Phos (758 mg, 1.85 mmol) was added and the mixture was refluxed for 48 h. After hydrolysis with water (50 mL), the mixture was extracted with ethyl acetate (2×100 mL), washed with brine (100 mL) and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure, and the crude material was purified by recrystallisation from methanol and washed with cold methanol. Yield:



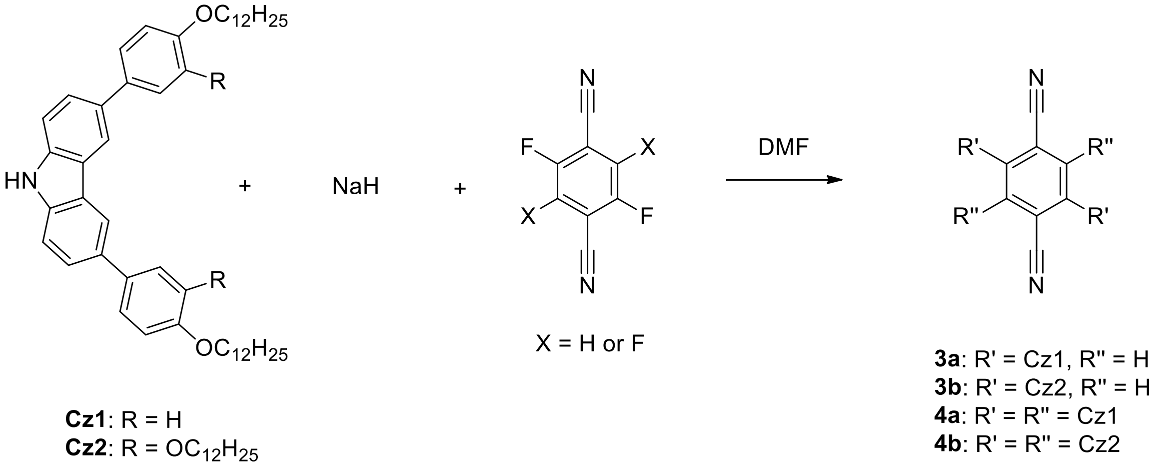
24.4 % (0.659 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.30 (2H, d, J = 1.8 Hz, Cz), 8.19 (1H, broad, NH), 7.66 (2H, dd, J = 8.4, 1.8 Hz, Cz), 7.50 (2H, d, J = 8.4 Hz, Cz), 7.27 (4H, m, Ph), 7.01 (2H, d, J = 8.3 Hz, Ph), 4.03 (6H, s, OCH$_3$), 3.97 (6H, s, OCH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.3, 148.2, 139.3, 135.3, 133.2, 125.6, 124.1, 119.6, 118.7, 111.7, 111.0, 110.9, 56.2.

2,5-Difluoro-1,4-dicyanobenzene



A mixture of 1,4-dibromo-2,5-difluorobenzene (1 g, 3.6 mmol), CuCN (1.65 g, 18.4 mmol) and Pd(PPh$_3$)$_4$ (0.43 g, 0.37 mmol) were placed in a Schlenk tube equipped with a stirrer and the system was evacuated and filled with nitrogen in 3 cycles. After extra dry dimethylformamide (20 mL) and pyridine (0.3 mL, 3.6 mmol) were added, the mixture was heated under a nitrogen atmosphere for 36 h. The reaction was quenched using 10% aq. NH$_3$ (20 mL), and the crude products were extracted with chloroform. The combined organic layers were washed with 10% aq. NH$_4$Cl (2x50 mL) and dried over anhydrous MgSO$_4$. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, dichloromethane). Yield: 26 % (160 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55 (2H, t, J = 6.2 Hz). ^{19}F NMR (376 MHz, CDCl$_3$): δ 108.42 (t, J = 5.8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 158.7 (dd, $^1J_{CF}$ = 262 Hz, $^4J_{CF}$ = 4.8 Hz), 121.4 (m, $^2J_{CF}$ and $^3J_{CF}$), 111.3 (CN), 107.7 (dd, $^2J_{CF}$ = 16 Hz, $^3J_{CF}$ = 12 Hz). MS (EI+(eiFi): C$_8$H$_2$N$_2$F$_2$ 164.0181, found 164.0174.

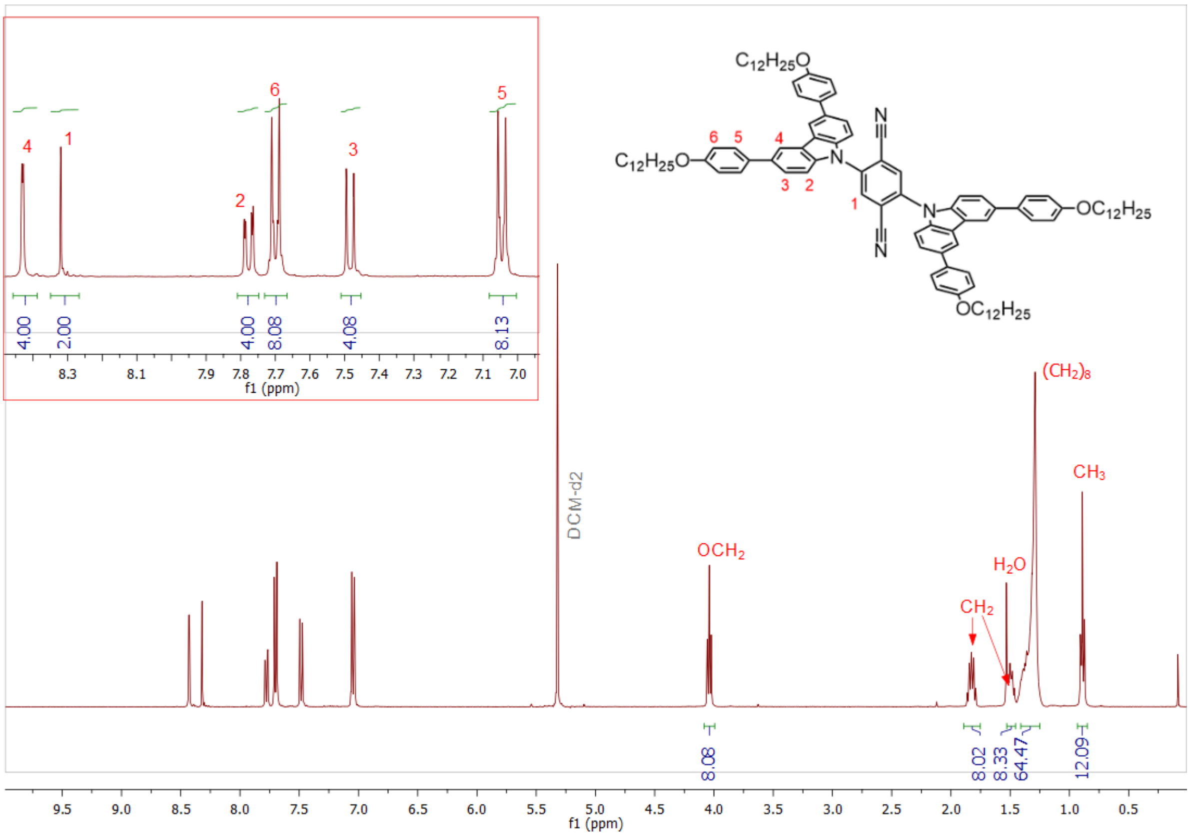
General procedure. Di- and tetrasubstituted terephthalonitriles (3a-4b)

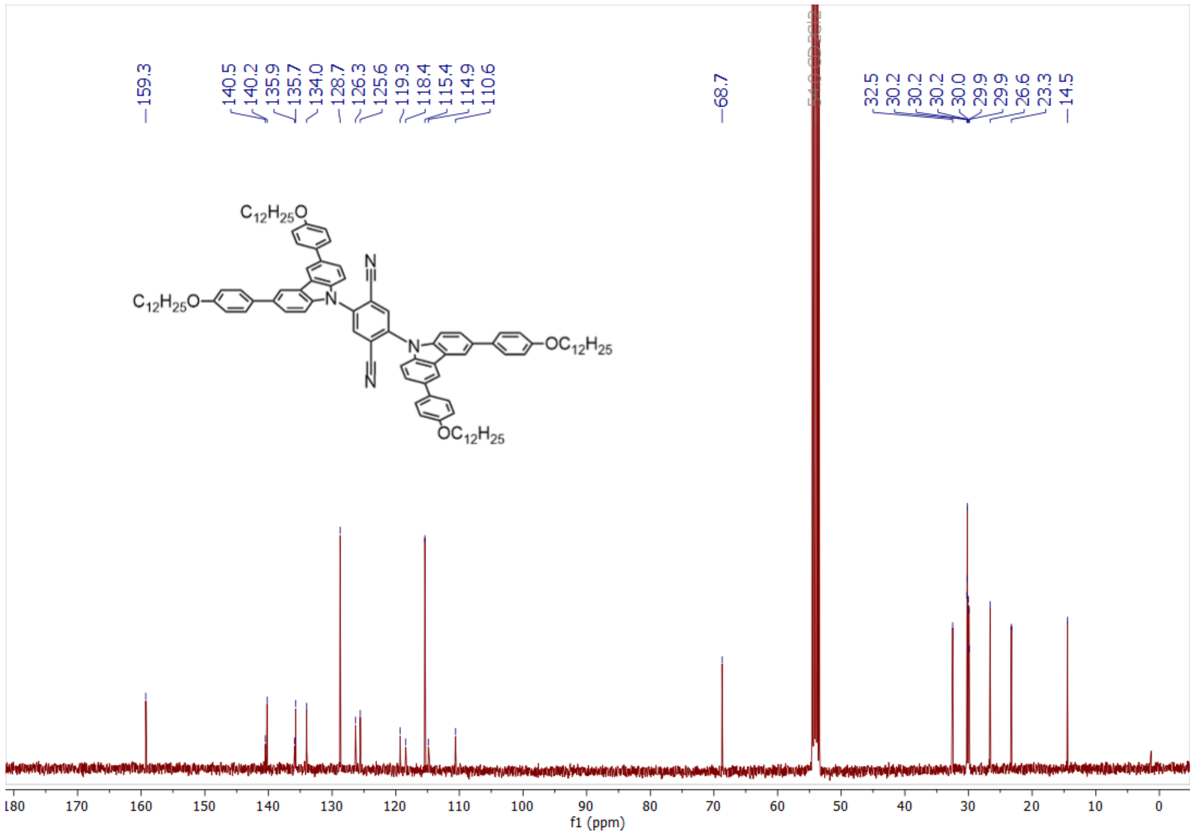


Sodium hydride (60% dispersion in oil) was washed with anhydrous hexane for 15 min. To this white powder, carbazole in extra dry dimethylformamide was added. After the liberation of H$_2$ gas had ceased, the yellow reaction mixture was stirred for 2 h at 70 °C. Then, terephthalonitrile in extra dry dimethylformamide was added. The reaction mixture was stirred for 4 h at 75 °C. The mixture has been cooled to ambient temperature, the precipitate was filtered off and washed with methanol. A product was purified by column chromatography.

2,5-Bis-(3,6-di-(4-dodecyloxyphenyl)carbazolyl)-1,4-dicyanobenzen (3a)

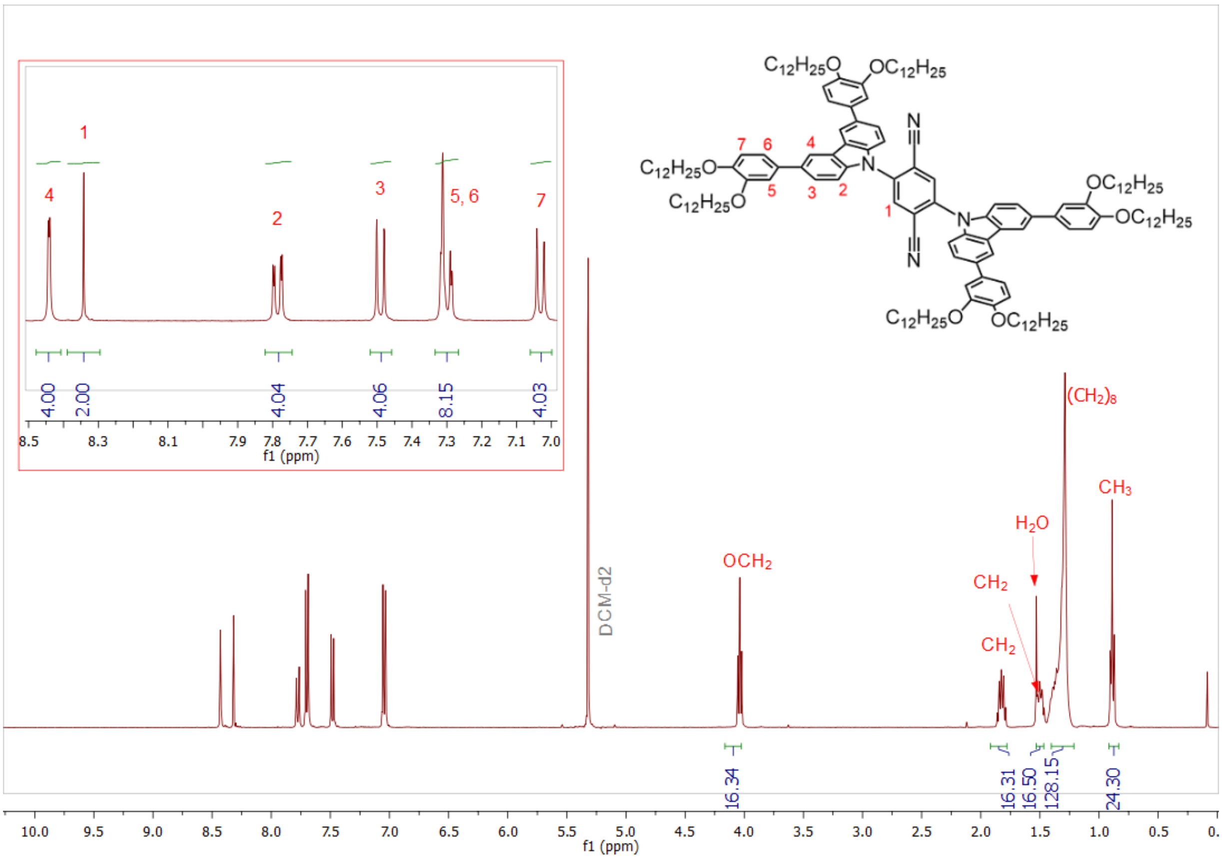
Purified by column chromatography (silica gel, dichloromethane/petroleum ether, 3/2). Yield: 66% (60 mg). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.43 (4 H, d, J = 1.8 Hz, Cz), 8.32 (2H, s, TPN), 7.77 (4H, dd, J = 8.8 Hz, 1.8 Hz, Cz), 7.70 (8 H, d, J = 8.7 Hz, Ph), 7.48 (4H, d, J = 8.8 Hz, Cz), 7.04 (8H, d, J = 8.7 Hz, Ph), 4.04 (8H, t, J = 6.6 Hz, OCH_2), 1,83 (8H, m, CH_2), 1.50 (8H, m, CH_2), 1.29 (64H, m, alkyl), 0.89 (12H, t, J = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 159.3, 140.5, 140.2, 135.9, 135.7, 134.0, 128.7, 126.3, 125.6, 119.3, 118.4, 115.4, 114.9, 110.6, 68.7, 32.5, 30.2, 30.2, 30.2, 30.0, 29.9, 29.9, 26.6, 23.3, 14.5. Anal. Calcd for $C_{104}H_{130}N_4O_4xH_2O$: C, 82.3; H, 8.8; N, 3.7. Found: C, 82.7; H, 8.5; N, 3.6%. MS (MALDI): $C_{104}H_{130}N_4O_4$, 1499.0087, found 1499.0116.





2,5-Bis-(3,6-di-(3,4-didodecyloxyphenyl)carbazolyl)-1,4-dicyanobenzene (3b)

Purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 9/1). Yield: 65% (443 mg). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.44 (4 H, d, J = 1.8 Hz, Cz), 8.34 (2H, s, TPN), 7.78 (4H, dd, J = 8.8 Hz, 1.8 Hz, Cz), 7.49 (4 H, d, J = 8.4 Hz, Cz, Ph), 7.30 (8H, m, Ph), 7.03 (4H, d, J = 8.0 Hz, Ph), 4.12 (8H, t, J = 6.6 Hz, OCH_2), 4.06 (8H, t, J = 6.6 Hz, OCH_2), 1,84 (16H, m, CH_2), 1.52 (16H, m, CH_2), 1.28 (128H, m, alkyl), 0.88 (24H, m, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 150.1, 149.4, 140.5, 140.3, 136.0, 135.9, 134.7, 126.5, 125.5, 125.4, 120.2, 119.5, 118.4, 114.8, 113.9, 110.6, 70.1, 69.9, 32.5, 30.3, 30.2, 30.1, 30.05, 30.0, 29.9, 26.7, 23.3, 14. Anal. Calcd for $C_{152}H_{226}N_4O_8$: C, 81.6; H, 10.2; N, 2.5; found: C, 81.2; H, 10.1; N, 2.4%. MS (MALDI): $C_{152}H_{226}N_4O_8$, 2235.7395, found 2235.7276.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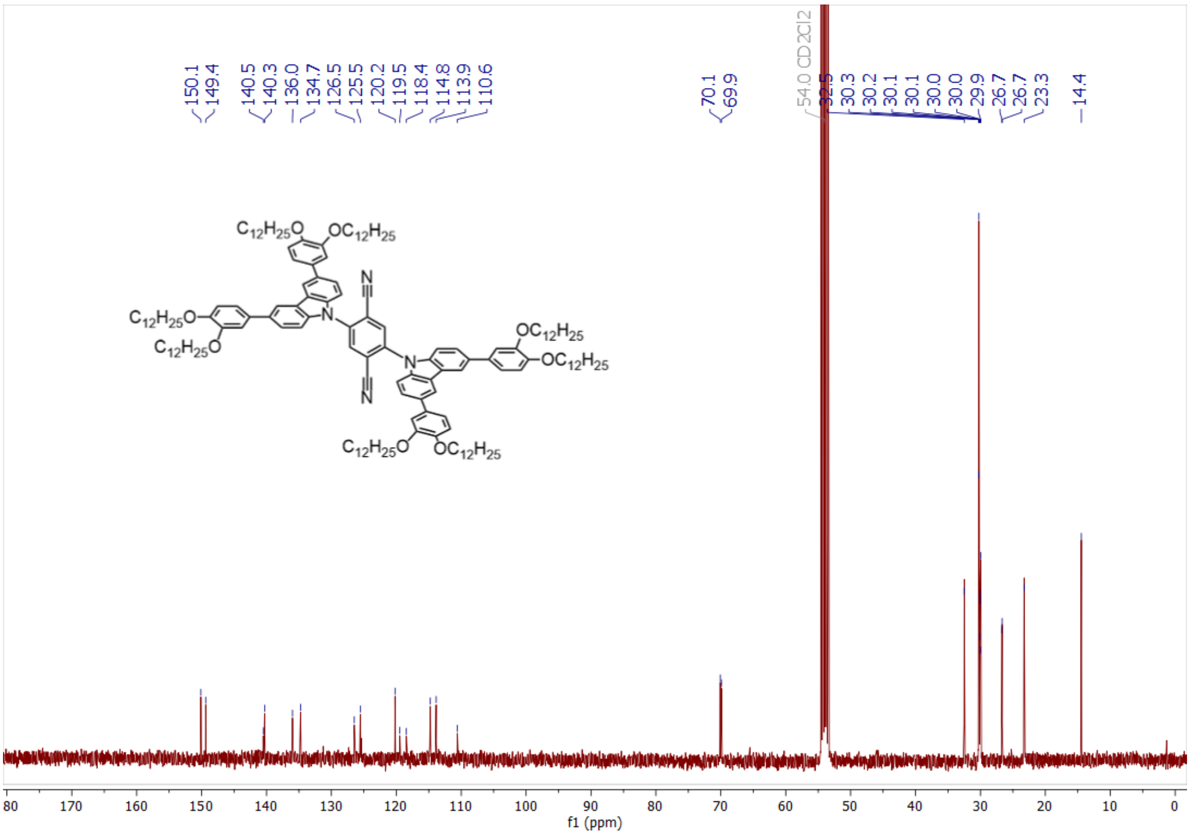
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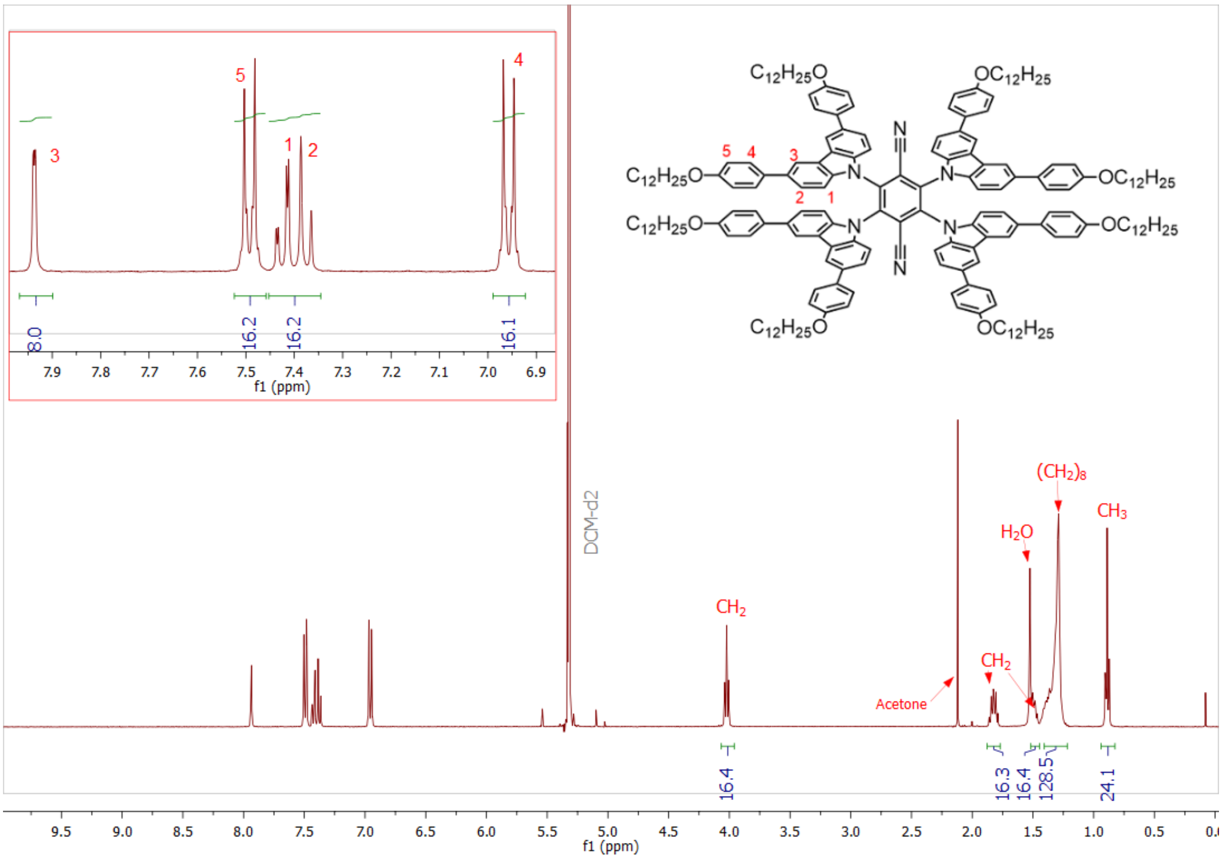
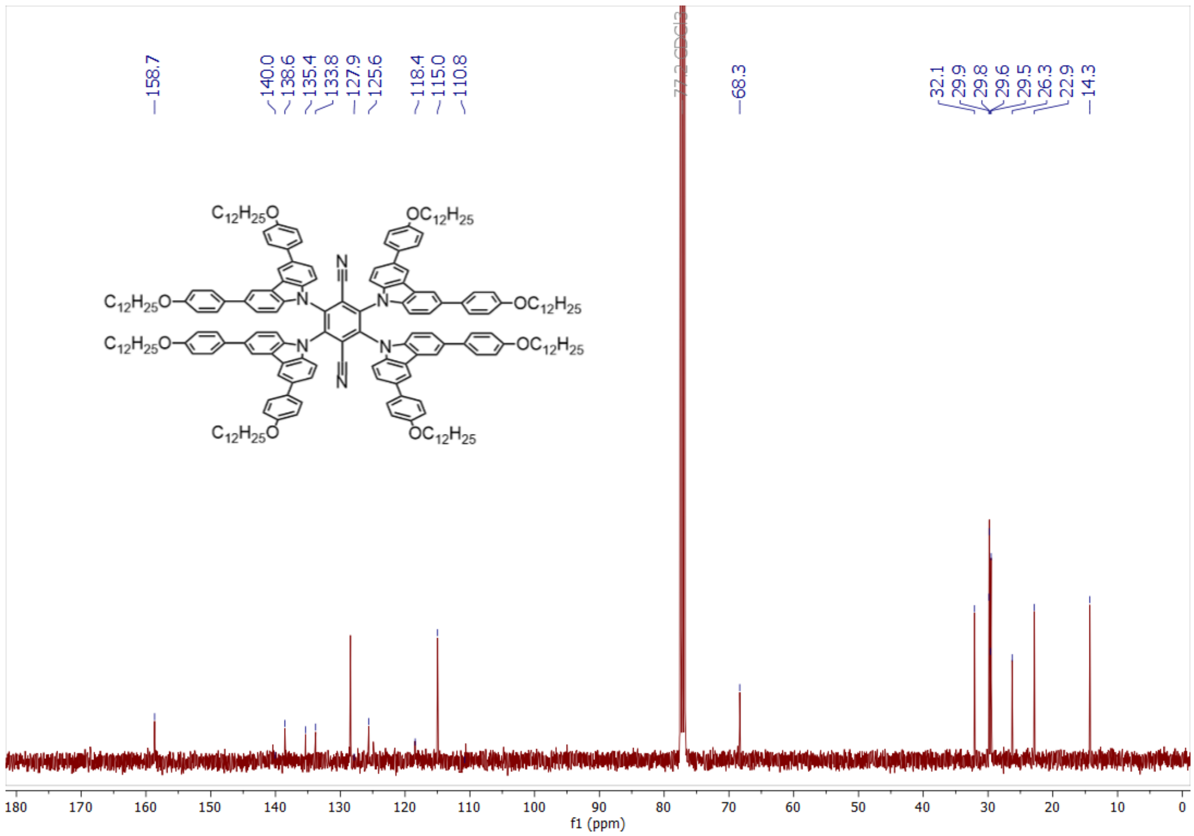
30.0
30.0
29.9
26.7
26.7
23.3
14.4
$C_{12}H_{25}O$
$OC_{12}H_{25}$
N
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2,3,5,6-Tetra(3,6-di-(4-dodecyloxyphenyl)carbazolyl)-1,4-dicyanobenzen (4a)

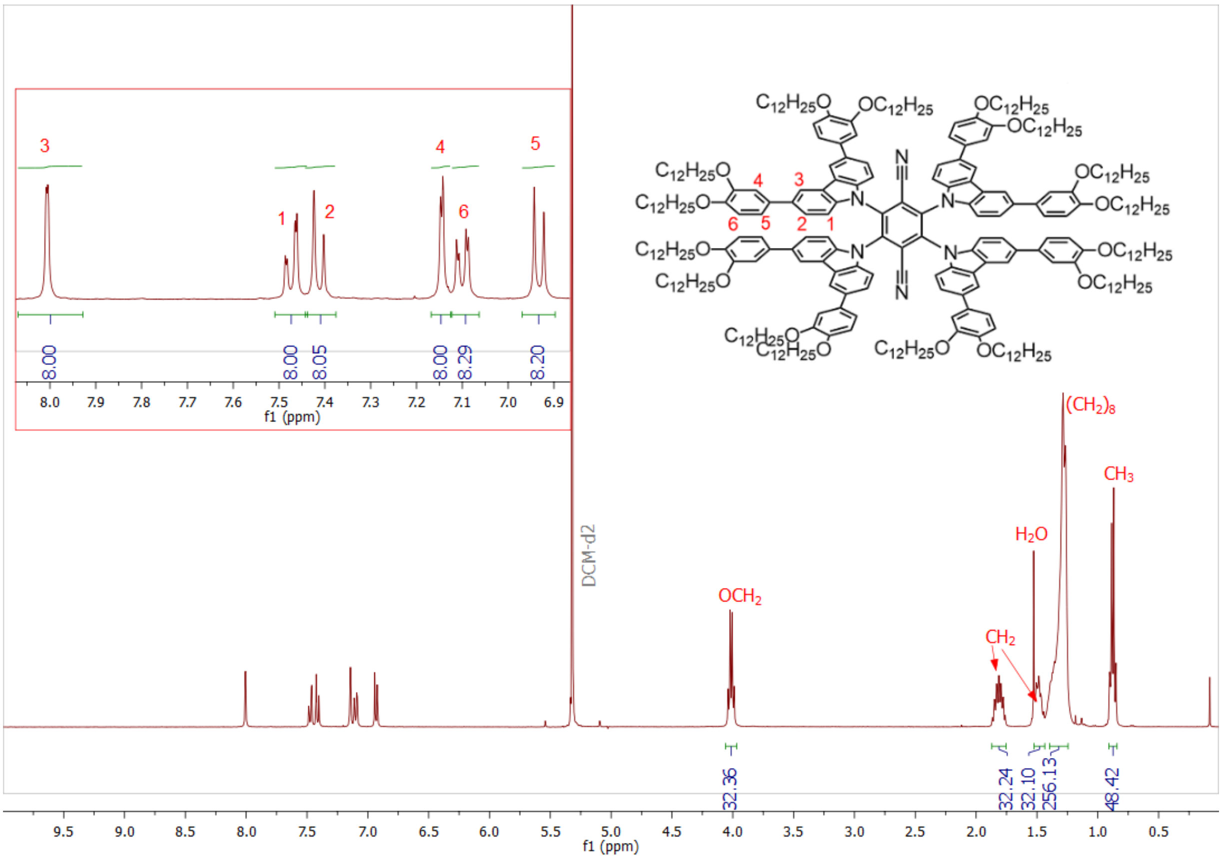
Purified by column chromatography (silica gel, dichloromethane/petroleum ether, 1/1), and slowly crystallised from an acetonitrile/dichloromethane solution. Yield: 10% (21 mg). ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 7.93 (8 H, d, *J* = 1.8 Hz, Cz), 7.49 (16H, d, *J* = 8.8 Hz, Ph), 7.42 (8 H, dd, *J* = 8.4 Hz, 1.8 Hz, Cz), 7.37 (8H, d, *J* = 8.4 Hz, Cz), 6.95 (16H, d, *J* = 8.8 Hz, Ph), 4.02 (16H, t, *J* = 6.6 Hz, OCH_2), 1,82 (16H, m, CH_2), 1.50 (16H, m, CH_2), 1.29 (128H, m, alkyl), 0.88 (24H, t, *J* = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 140.5, 138.6, 135.4, 133.8, 128.4, 125.6, 124.9, 118.4, 115.0, 110.6, 68.3, 32.1, 29.9, 29.8, 29.6, 29.5, 26.3, 22.9, 14.3. Anal. Calcd for $C_{200}H_{256}N_6O_8xH_2O$: C, 83.1; H, 9.0; N, 2.9. Found: C, 82.7; H, 8.7; N, 2.6%. MS (MALDI): $C_{200}H_{256}N_6O_6$, 2869.9804, found 2869.9886.

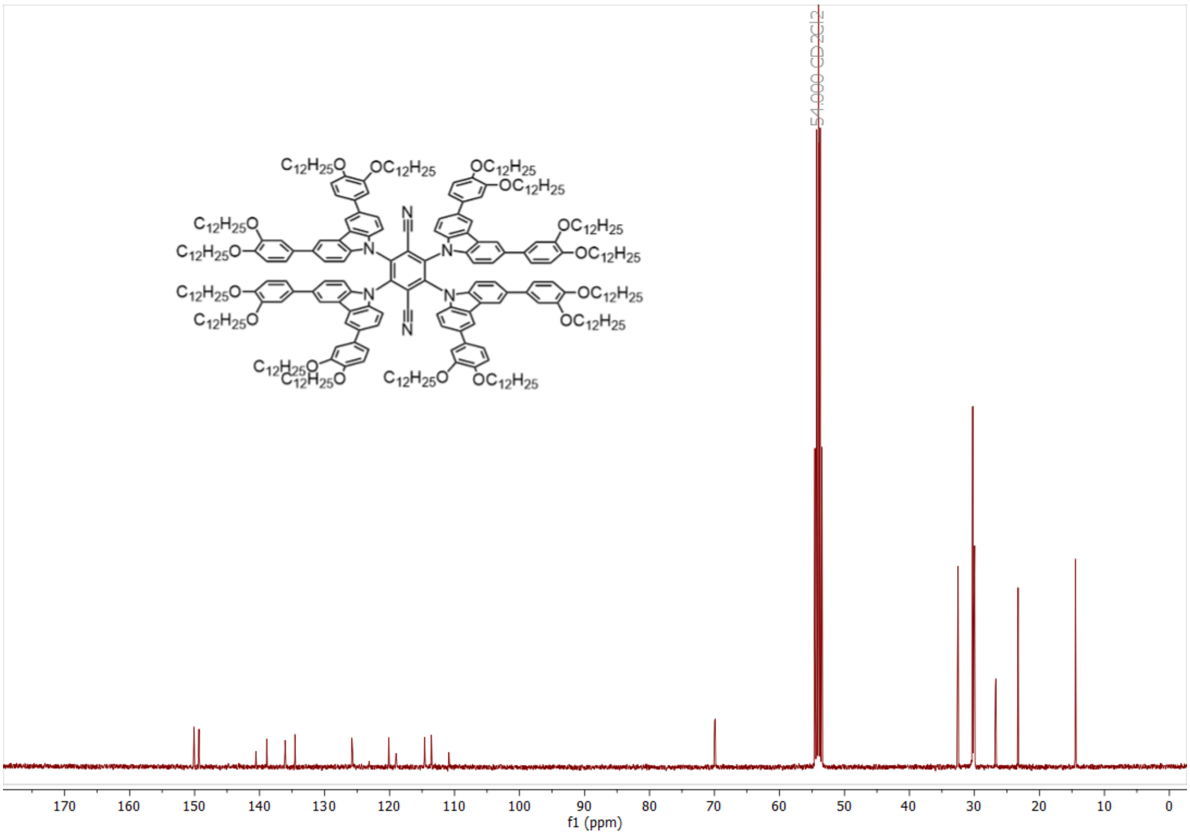




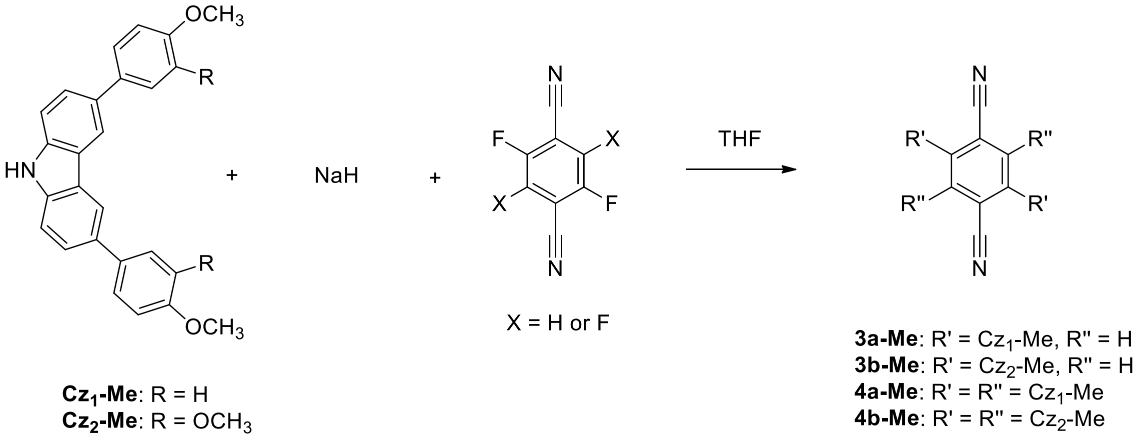
2,3,5,6-Tetra(3,6-di-(3,4-didodecyloxyphenyl)carbazolyl)-1,4-dicyanobenzen (4b)

Purified by column chromatography (silica gel, dichloromethane/petroleum ether, 1/1). Yield: 23% (60 mg). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.00 (8 H, d, J = 1.8 Hz, Cz), 7.47 (8 H, dd, J = 8.6 Hz, 1.8 Hz, Cz), 7.41 (8H, d, J = 8.6 Hz, Cz), 7.14 (8H, d, J = 2.2 Hz, Ph), 7.10 (8H, dd, J = 8.3, 2.2 Hz, Ph), 6.93 (8H, d, J = 8.3 Hz, Ph), 4.01 (32H, m, OCH_2), 1,81 (32H, m, CH_2), 1.48 (32H, m, CH_2), 1.29 (256H, m, alkyl), 0.88 (48H, m, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 150.1, 149.3, 140.6, 138.9, 136.1, 134.6, 125.8, 125.7, 120.1, 119.0, 114.6, 113.6, 110.9, 70.0, 69.9, 32.5, 30.3, 30.3, 30.3, 30.3, 30.1, 30.1, 30.0, 30.0, 26.8, 26.7, 23.3, 14.5. Anal. Calcd for $C_{296}H_{448}N_6O_{16}$: C, 81.8; H, 10.4; N, 1.9; found: C, 81.7; H, 10.7; N, 2.0%. MS (MALDI): $C_{296}H_{449}N_6O_{16}$, 4344.4499, found 4344.4286.


3
1
2
4
6
5
8.00
8.00
8.05
8.00
8.29
8.20
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
$C_{12}H_{25}O$
$OC_{12}H_{25}$
N
DCM-d2
OCH_2
CH_2
H_2O
$(CH_2)_8$
CH_3
32.36
32.24
32.10
256.13
48.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


54.000 CD2Cl2
$C_{12}H_{25}O$
$OC_{12}H_{25}$
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

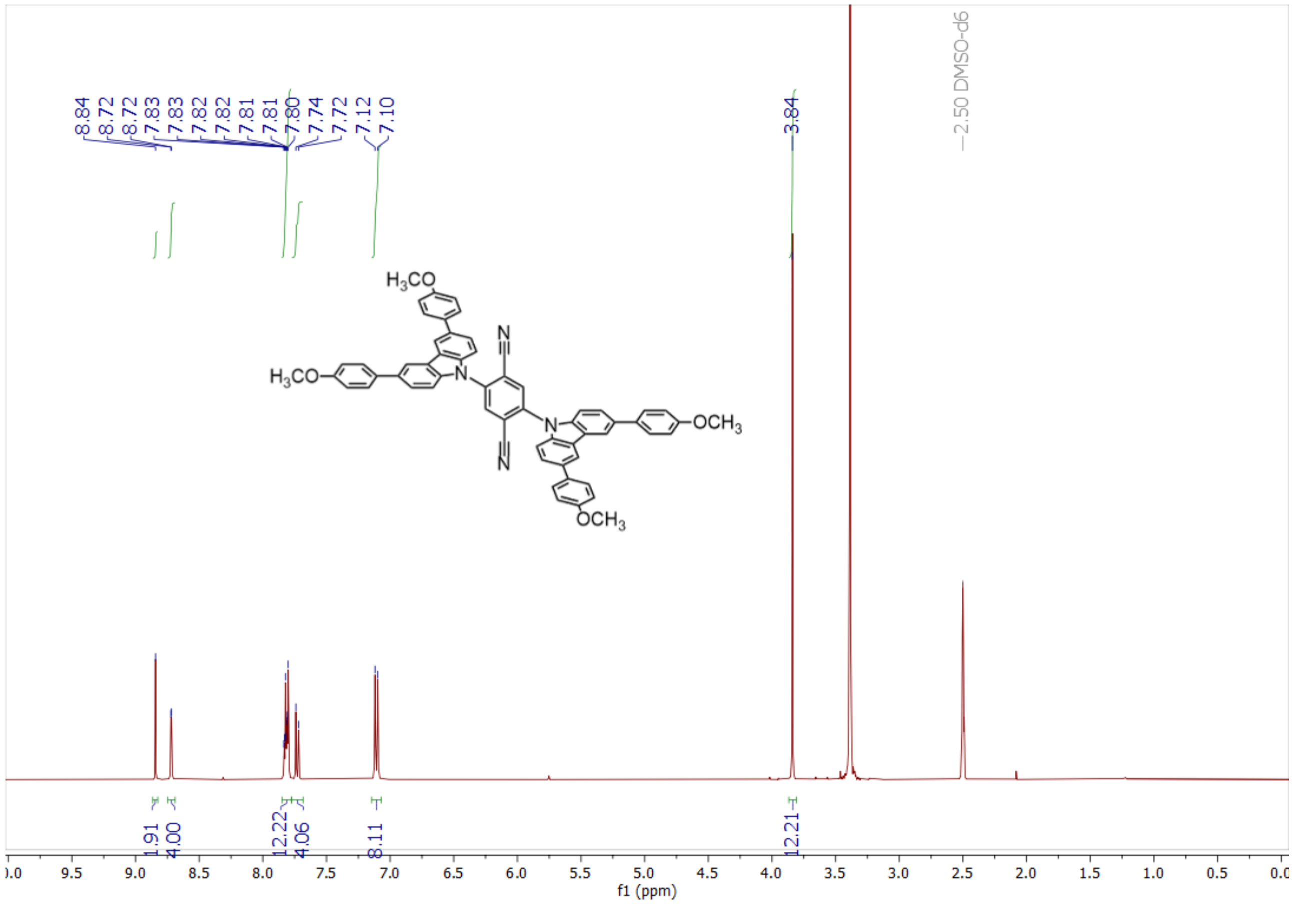
General procedure. Methoxy analogues of di- and tetrasubstituted terephthalonitriles (3a-Me – 4b-Me)

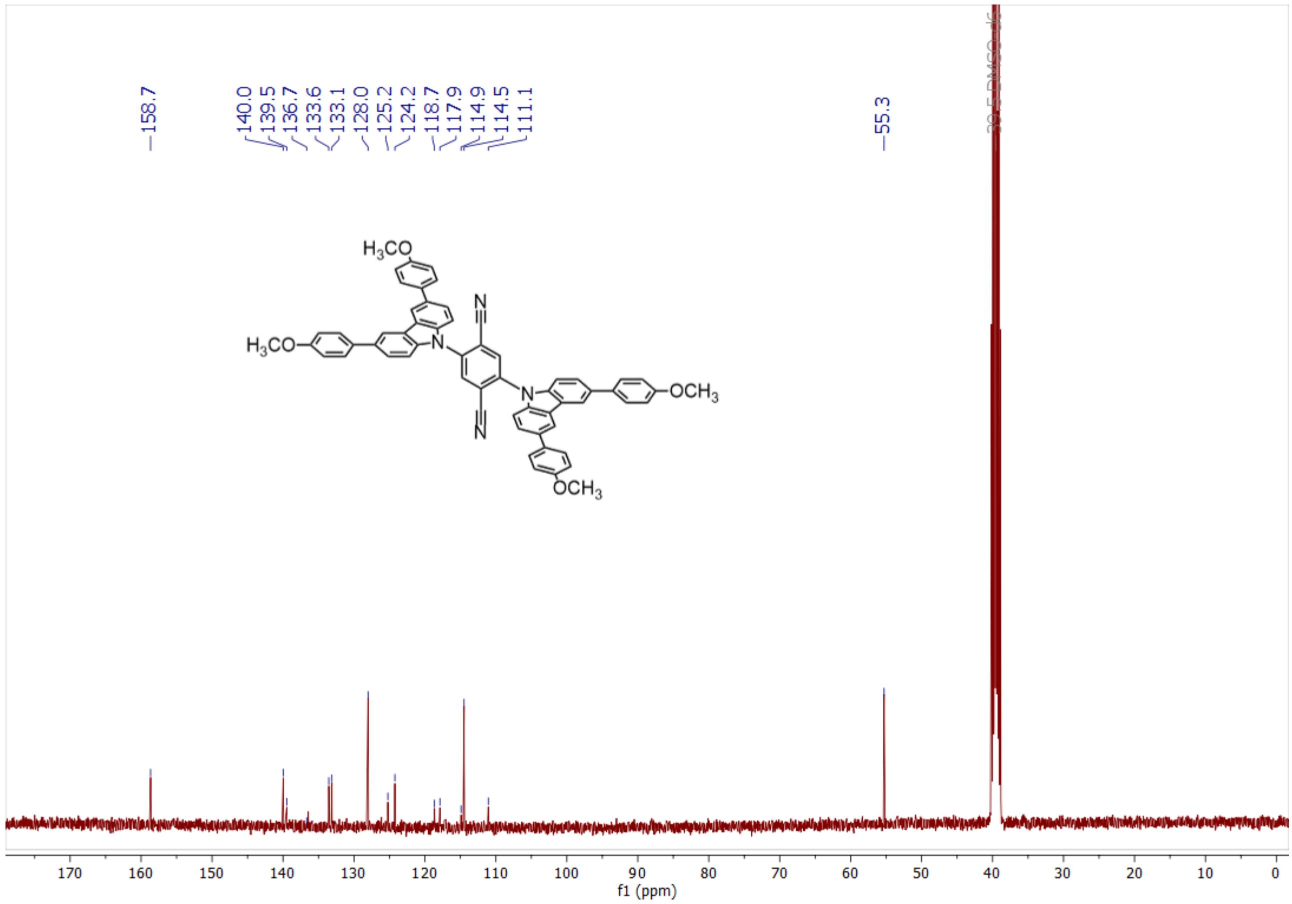


Sodium hydride (60% dispersion in oil) was washed with anhydrous hexane for 15 min. To this white powder, carbazole in extra dry tetrahydrofuran was added. The yellow reaction mixture was stirred for 2 h at 70 °C. Then, terephthalonitrile in dry tetrahydrofuran was added. The reaction mixture was stirred at 75 °C overnight. Water was added to the mixture. The mixture was extracted with dichloromethane, washed with brine and dried over anhydrous $MgSO_4$. Solvents were evaporated. A product was purified by column chromatography.

2,5-Bis-(3,6-di-(4-methoxyphenyl)carbazolyl)-1,4-dicyanobenzene (3a-Me)

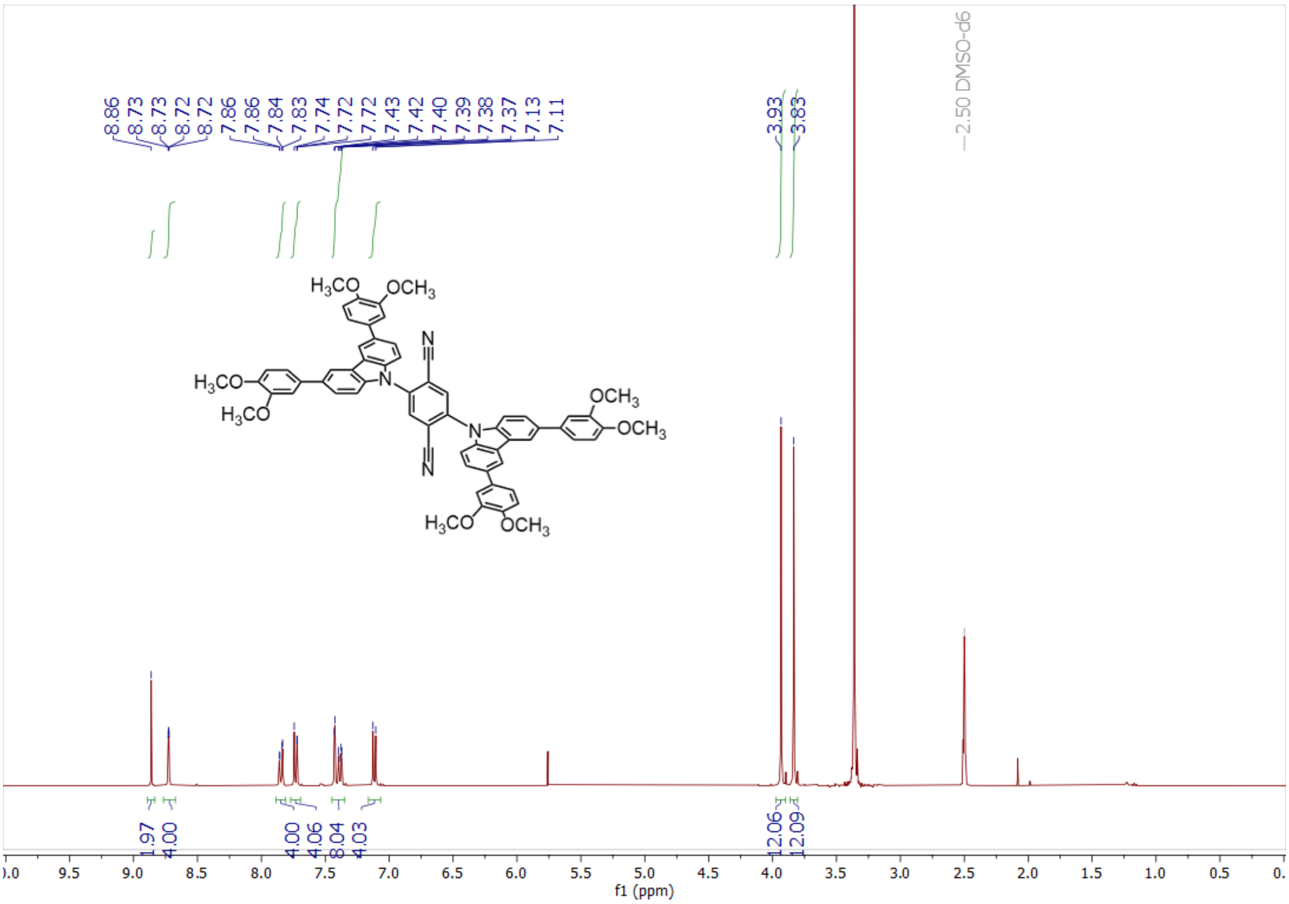
Purified by column chromatography (silica gel, dichloromethane). Yield: 17% (57 mg). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.84 (2H, s, TPN), 8.72 (4 H, d, J = 1.8 Hz, Cz), 7.82 (4H, dd, J = 8.6, 1.8 Hz, Cz), 7.81 (8H, d, J = 8.8 Hz, Ph), 7.73 (4H, d, J = 8.6 Hz, Cz), 7.10 (8H, d, J = 8.8 Hz, Ph), 3.84 (12H, s, OCH_3). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 158.7, 140.0, 139.5, 136.4, 133.5, 133.1, 128.0, 125.2, 124.2, 118.7, 117.9, 114.9, 114.5, 111.1, 55.3.

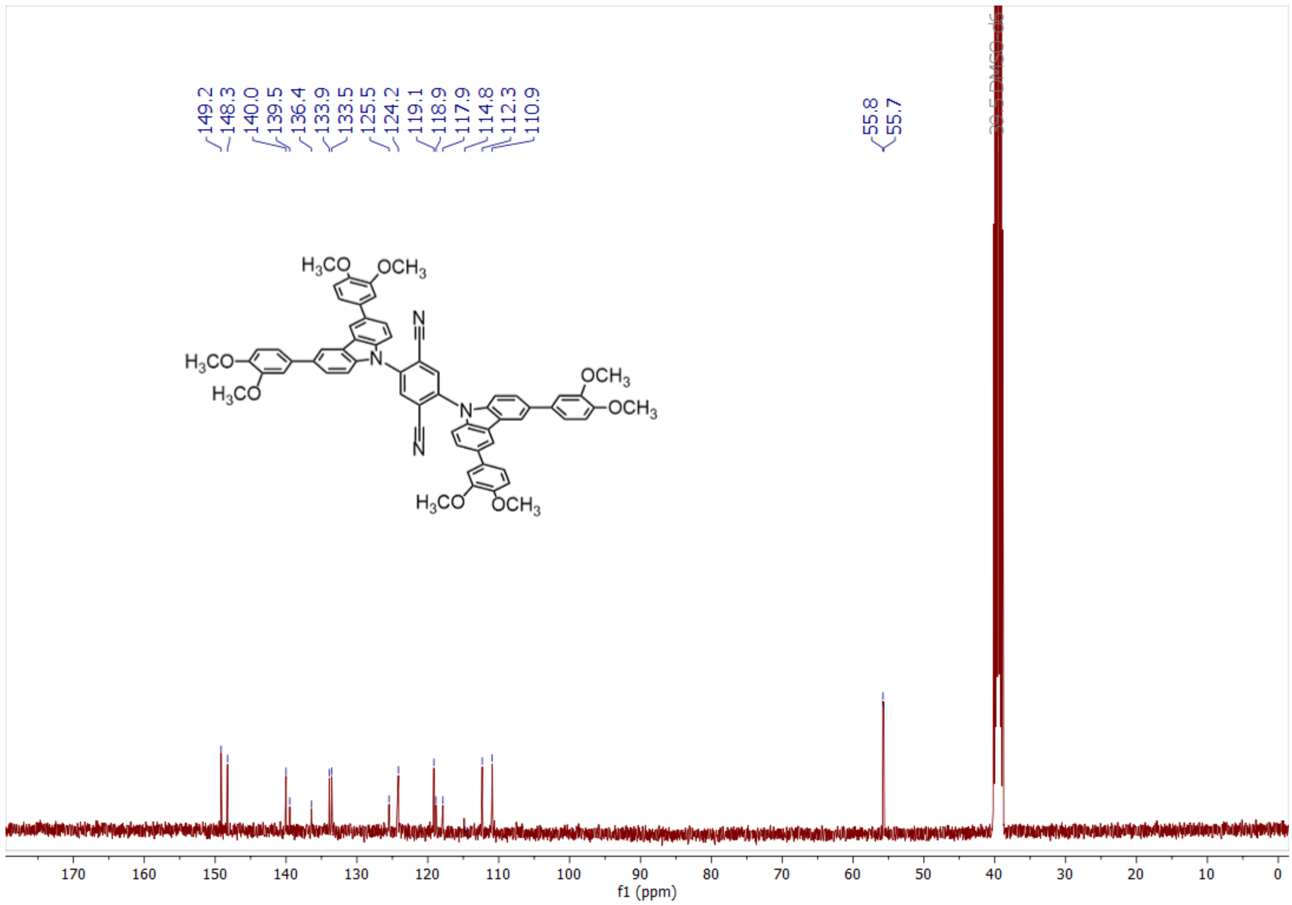

8.84
8.72
8.72
7.83
7.83
7.82
7.82
7.81
7.81
7.80
7.74
7.72
7.12
7.10
3.84
2.50 DMSO-d6
H3CO
H3CO
N
N
N
N
OCH3
OCH3
1.91
4.00
12.22
4.06
8.11
12.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.7
140.0
139.5
136.7
133.6
133.1
128.0
125.2
124.2
118.7
117.9
114.9
114.5
111.1
55.3
39.5 DMSO-d6
H3CO
H3CO
N
N
N
N
OCH3
OCH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2,5-Bis-(3,6-di-(3,4-dimethoxyphenyl)carbazolyl)-1,4-dicyanobenzene (3b-Me)

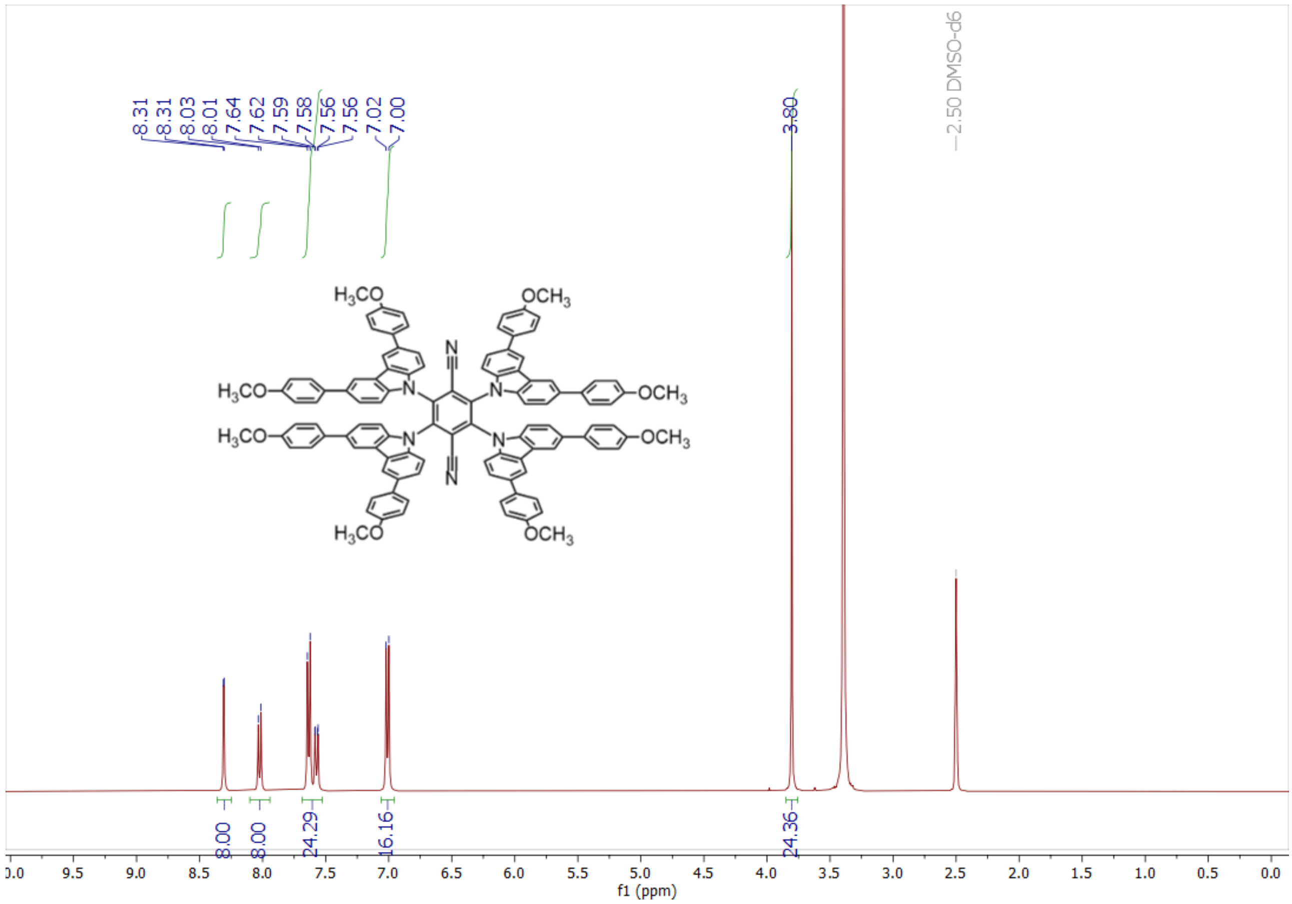
Purified by column chromatography (silica gel, dichloromethane/ethyl acetate). Yield: 28 % (105 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.85 (2H, s, TPN), 8.72 (4 H, d, J = 1.8 Hz, Cz), 7.84 (4H, dd, J = 8.6, 1.8 Hz, Cz), 7.72 (4H, d, J = 8.6 Hz, Cz), 7.42 (4 H, d, J = 2.2 Hz, Ph), 7.38 (8H, dd, J = 8.3, 2.2 Hz, Ph), 7.11 (4H, d, J = 8.3 Hz, Ph), 3.93 (12H, s, OCH$_3$), 3.83 (12H, s, OCH$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.2, 148.3, 140.0, 139.5, 136.4, 133.9, 133.5, 125.5, 124.2, 119.1, 118.9, 117.9, 114.9, 112.3, 111.0, 110.9, 55.8, 55.7.

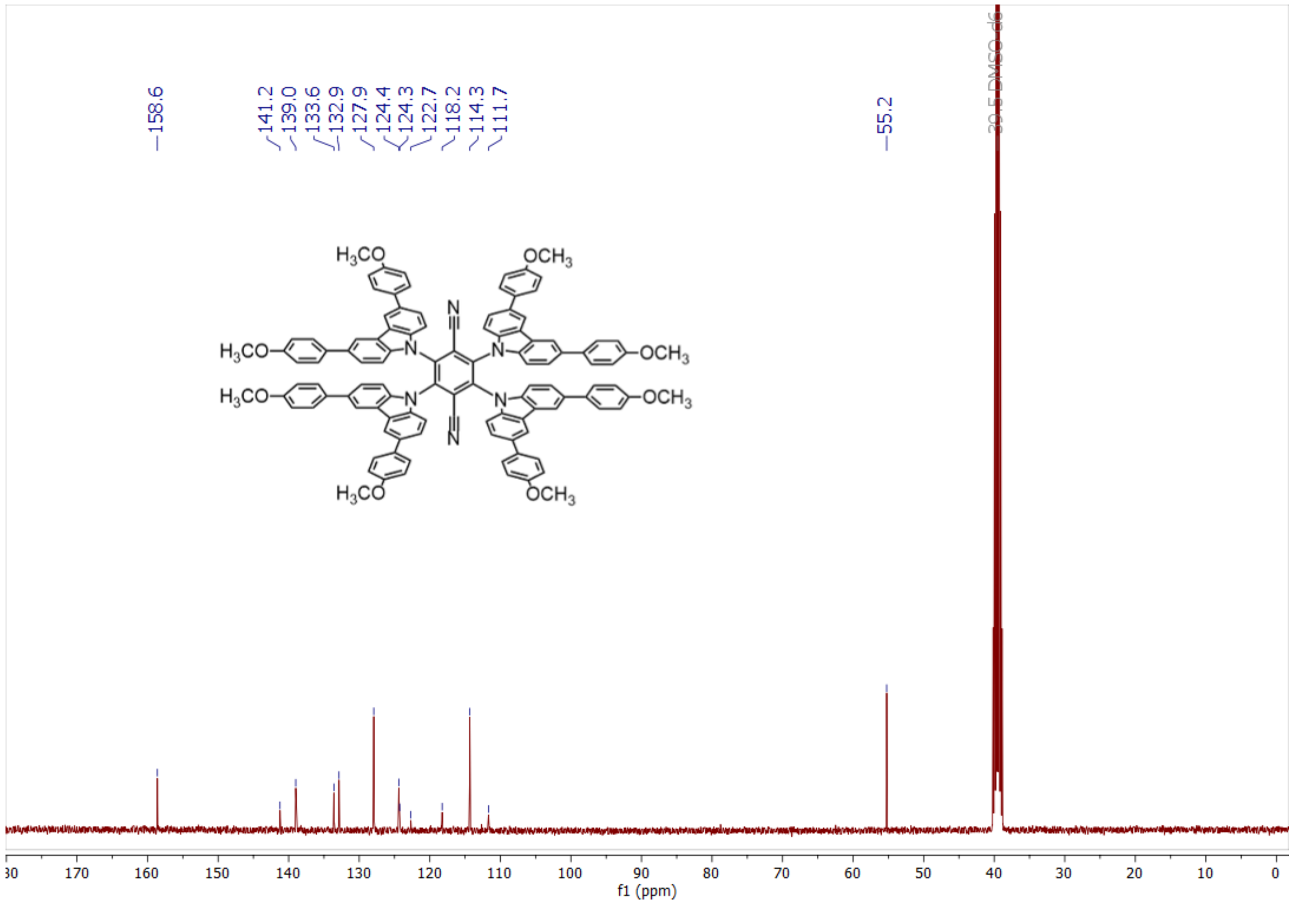




2,3,5,6-Tetra(3,6-di-(4-methoxyphenyl)carbazolyl)-1,4-dicyanobenzene (4a-Me)

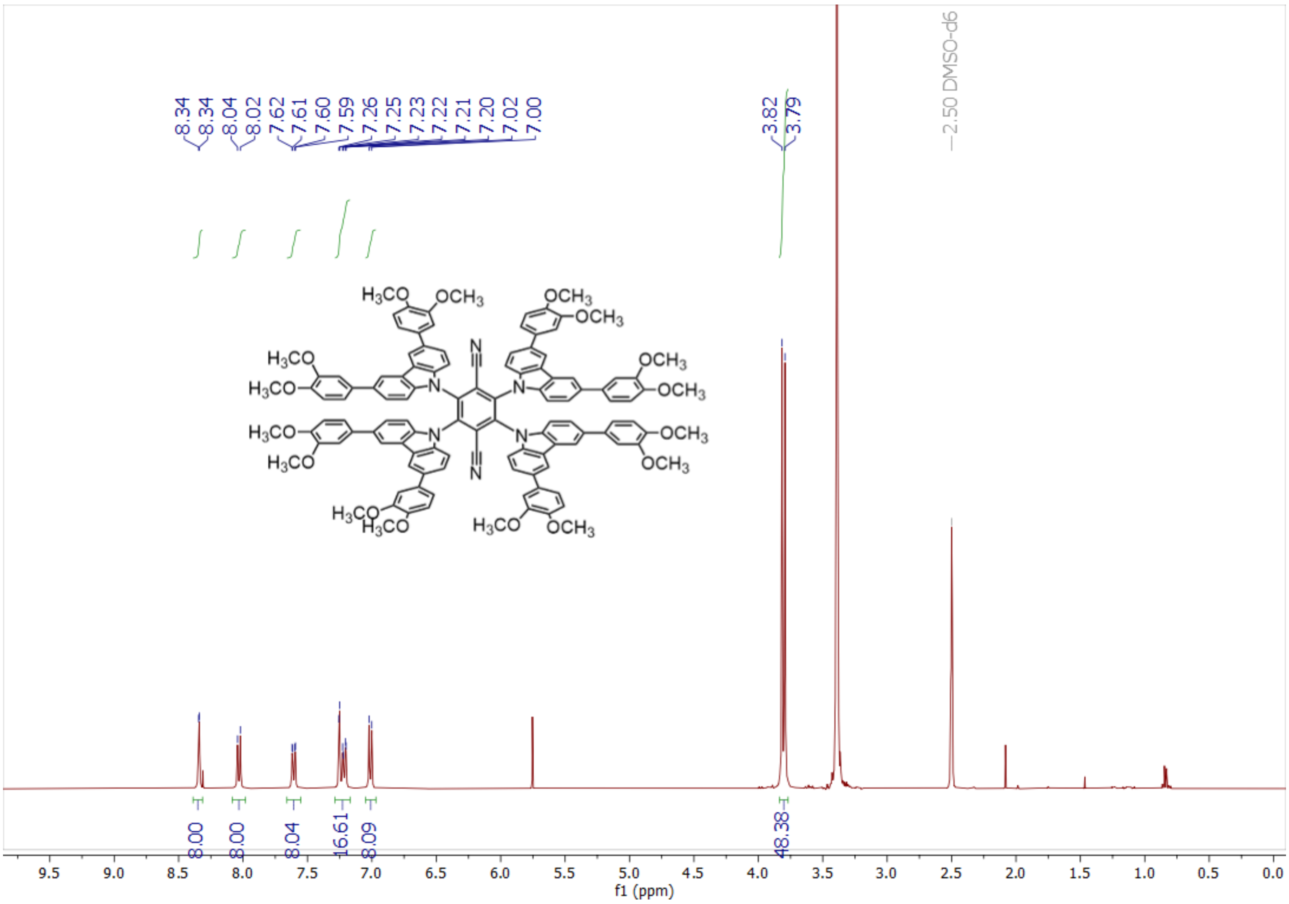
The precipitate was filtered off and washed with water and a hexane/acetone mixture (9/1). Yield: 55% (144 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.41 (8H, d, J = 1.8 Hz, Cz), 7.13 (8H, d, J = 8.6 Hz, Cz), 6.74 (16 H, d, J = 8.8 Hz, Ph), 6.68 (8H, dd, J = 8.6, 1.8 Hz, Cz), 6.11 (16H, d, J = 8.8 Hz, Ph), 2.91 (24H, s, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.6, 141.2, 139.0, 133.6, 132.9, 127.9, 124.4, 124.3, 122.7, 118.2, 114.3, 111.7, 55.2.

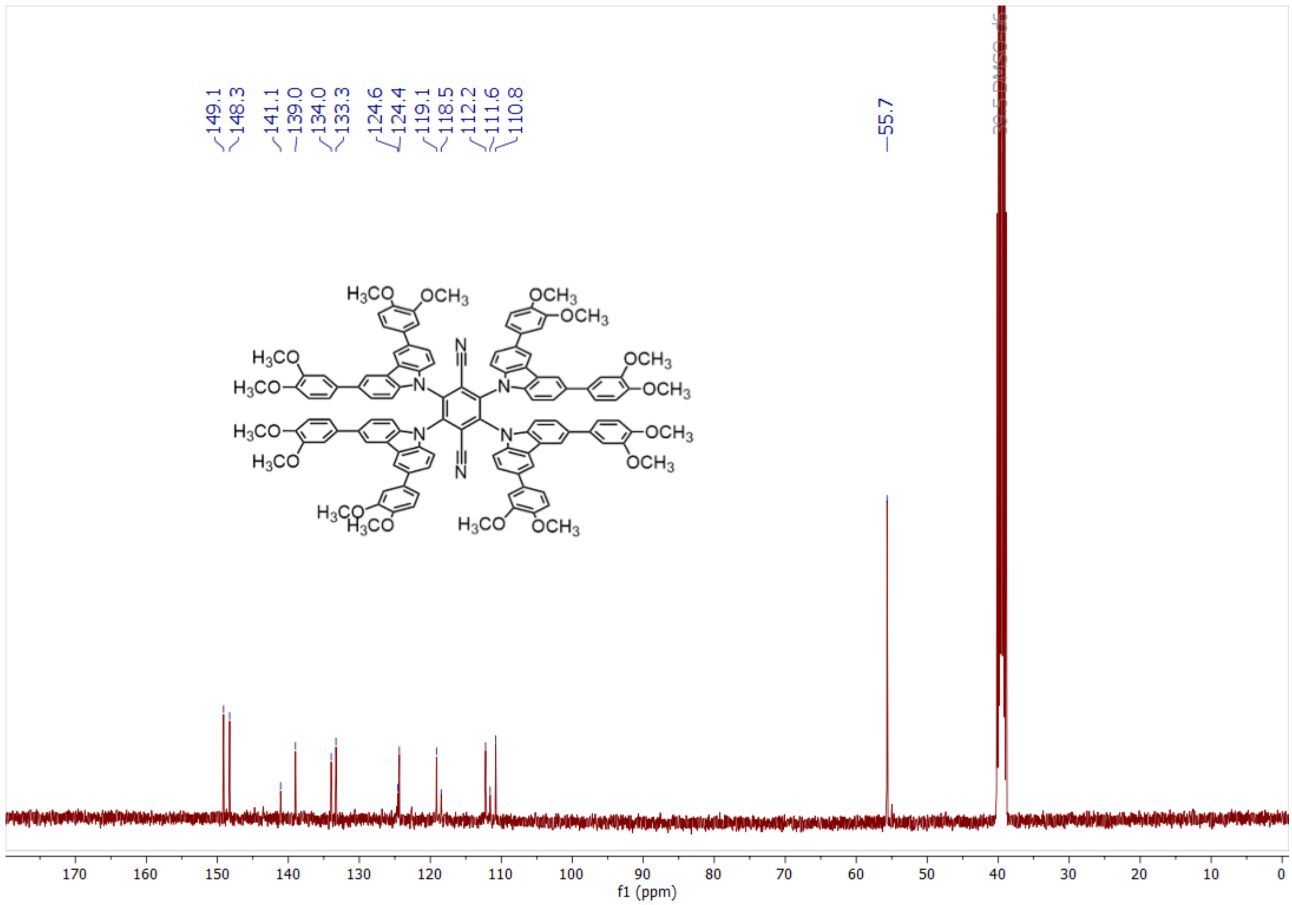

8.31
8.31
8.03
8.01
7.64
7.62
7.59
7.58
7.56
7.56
7.02
7.00
3.80
2.50 DMSO-d6
H3CO
OCH3
H3CO
OCH3
H3CO
OCH3
H3CO
OCH3
N
N
N
N
N
N
8.00
8.00
24.29
16.16
24.36
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.6
141.2
139.0
133.6
132.9
127.9
124.4
124.3
122.7
118.2
114.3
111.7
55.2
39.5 DMSO-d6
H3CO
OCH3
H3CO
OCH3
H3CO
OCH3
H3CO
OCH3
N
N
N
N
N
N
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2,3,5,6-Tetra(3,6-di-(3,4-dimethoxyphenyl)carbazolyl)-1,4-dicyanobenzene (4b-Me)

The precipitate was filtered off and washed with water and a hexane/acetone mixture (9/1). Yield: 40% (124 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.34 (8 H, d, J = 1.8 Hz, Cz), 8.03 (8H, d, J = 8.6 Hz, Cz), 7.60 (8H, dd, J = 8.6, 1.8 Hz, Cz), 7.25 (8H, d, J = 2.0 Hz, Ph), 7.21 (8H, dd, J = 8.3, 2.0 Hz, Ph), 7.01 (8H, d, J = 8.3 Hz, Ph), 3.81 (24H, s, OCH$_3$), 3.79 (24H, s, OCH$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.1, 148.3, 141.1, 139.0, 134.0, 133.3, 124.6, 124.4, 119.1, 118.5, 112.2, 111.6, 110.8, 55.7.




149.1
148.3
141.1
139.0
134.0
133.3
124.6
124.4
119.1
118.5
112.2
111.6
110.8
55.7
39.5 DMSO-d6
H_3CO
OCH_3
H_3CO
H_3CO
H_3CO
H_3CO
H_3CO
H_3CO
H_3CO
OCH_3
OCH_3
OCH_3
OCH_3
OCH_3
OCH_3
OCH_3
N
N
N
N
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

X-ray Crystallographic Analyses

Table S1 Crystal data and structure refinement for Compounds **3b-Me** and **4b-Me**

	3b-Me	**4b-Me**
CCDC Number	2056911	2056912
Empirical formula	$C_{123.31}H_{99.31}Cl_{9.94}N_6O_{16.24}$	$C_{68}H_{56}N_6O_8$
Formula weight	2277.32	1085.18
Temperature/K	110.00(10)	110.00(10)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	11.3160(7)	8.7095(6)
b/Å	15.6983(10)	12.8934(10)
c/Å	16.1277(11)	14.2434(10)
α/°	73.671(6)	101.702(6)
β/°	86.678(5)	105.271(6)
γ/°	81.686(5)	108.031(7)
Volume/Å^3	2720.0(3)	1394.93(19)
Z	1	1
ρ_{calc} g/cm^3	1.390	1.292
μ/mm^{-1}	2.910	0.690
F(000)	1180.0	570.0
Crystal size/mm^3	0.144 × 0.091 × 0.01	0.245 × 0.062 × 0.03
Radiation	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7 to 134.158	6.766 to 134.136
Index ranges	$-13 \leq h \leq 12$, $-18 \leq k \leq 16$,	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$,
Reflections collected	16956	8913
Independent reflections	9662 [R_{int} = 0.0504,	4977 [R_{int} = 0.0273,
Data/restraints/parameters	9662/33/797	4977/3/468
Goodness-of-fit on F^2	1.012	1.028
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0568, wR_2 = 0.1373	R_1 = 0.0431, wR_2 = 0.1034
Final *R* indexes [all data]	R_1 = 0.0876, wR_2 = 0.1600	R_1 = 0.0612, wR_2 = 0.1144
Largest diff. peak/hole/e Å^{-3}	0.37/-0.42	0.38/-0.19

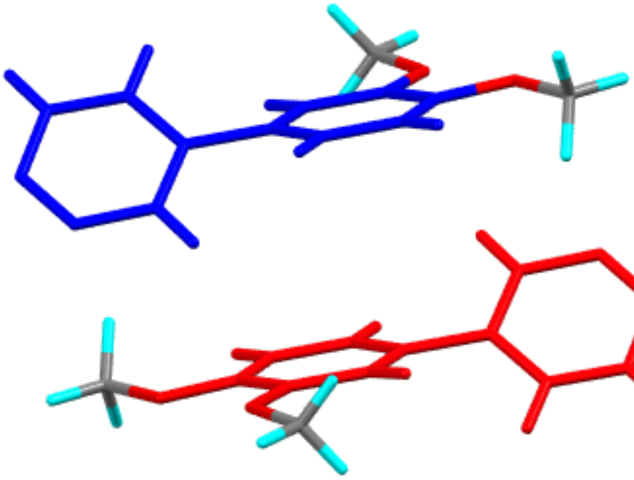


Figure S1 Figure showing the intermolecular disposition of dimethoxyphenyl units – separation between the rings is 3.985 Å.

Liquid Crystal Data

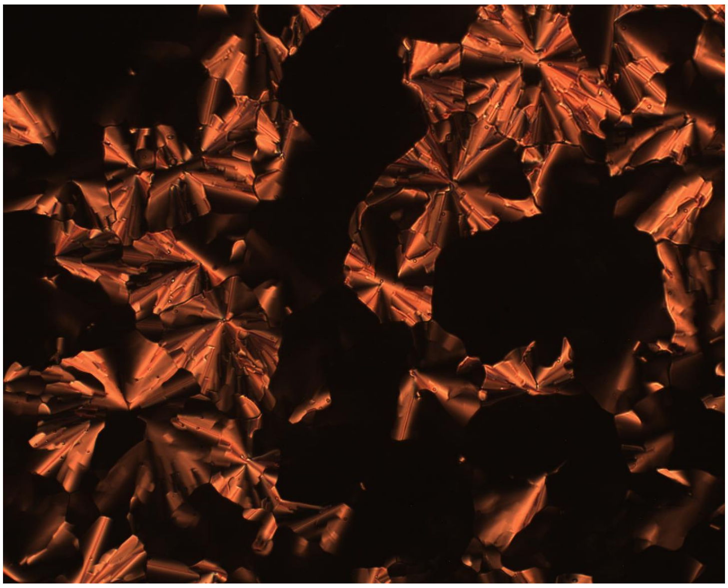


Figure S2 Col_h phase of a mixture of **3b** and **4b** at 150 °C on cooling from the isotropic phase in which the compounds were mixed.

Photophysical Data

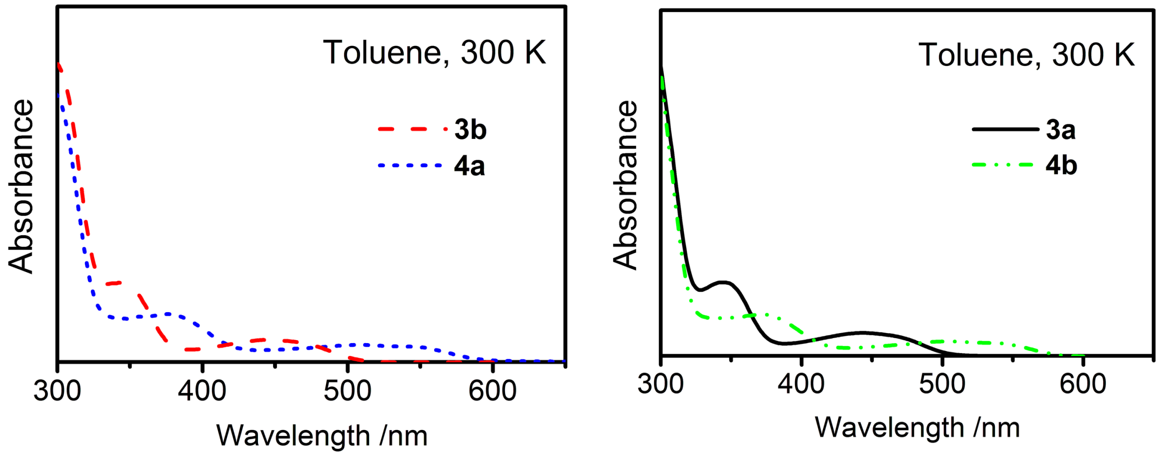


Figure S3. UV-Vis absorption spectra of compounds **3a, 3b**, **4a** and **4b** in toluene.

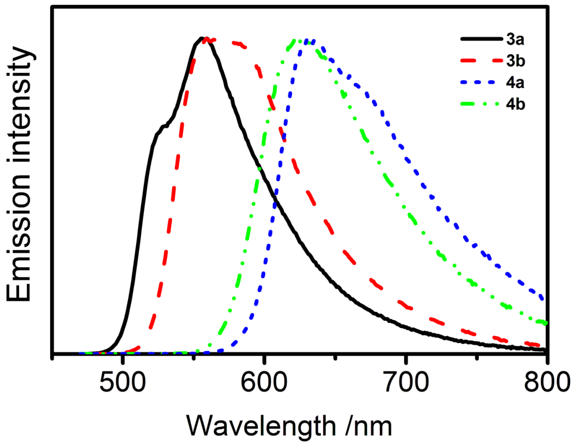


Figure S4 Luminescence spectra of solid samples of compounds **3a**, **3b**, **4a**, and **4b** at ambient temperature. Spectral forms of the recorded emission bands suggest significant inhomogeneity of the samples.

Table S2 Luminescence properties of compounds **3a**, **3b**, **4a**, and **4b** determined for solid samples at ambient temperature

	λ_{max} /nm	**τ /ns Prompt flu.**	**τ /µs Delayed em.**	**ϕ_{PL} /%**	**k_r /s^{-1}**	**k_{nr} /s^{-1}**
3a	554	13	27 (5% int)[a]	30 (27)	2.3×10^7	5.3×10^7
3b	560	10.7	18 (10% int)[a]	20 (18)	1.7×10^7	8.2×10^7
4a	625	3.6	1.1	11	3.1×10^7	25×10^7
4b	635	3.9	≤1	4	1.0×10^7	25×10^7

[a] 'int' refers to the % emission intensity arising from the longer-lived emission.

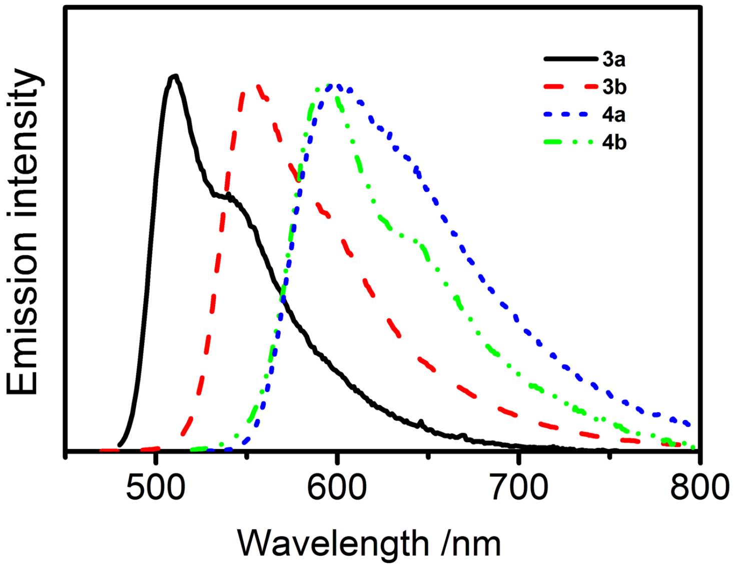


Figure S5. Luminescence spectra of compounds **3a**, **3b**, **4a**, and **4b** recorded in frozen toluene glass at 77K.

Table S2. Luminescence properties of compounds **3a**, **3b**, **4a**, and **4b** determined in toluene at 77 K

	λ_{max} /nm	τ /ns Prompt flu.	τ /µs Delayed em.	ϕ_{PL} /%	k_r /s^{-1}	k_{nr} /s^{-1}
3a	509	17	–	92	5.4×10^7	0.5×10^7
3b	554	12	–	25	2.1×10^7	6.3×10^7
4a	593	10.4	–	52	5.0×10^7	4.6×10^7
4b	601	7.7	–	17	2.2×10^7	11×10^7

Theoretical data

Table S3. DFT calculated frontier orbital energies and partial contributions of **3b-Me** in the state T_1 geometry resulting from Mulliken population analysis.

Orbitals	Energy, eV	Contributions, %	
		Terephthalonitrile	Methoxyphenyl substituted carbazoles
LUMO+4	-1.765	1	99
LUMO+3	-2.145	2	98
LUMO+2	-2.156	2	98
LUMO+1	-2.632	85	15
LUMO	-3.967	95	5
HOMO	-5.077	2	98
HOMO-1	-5.149	3	97
HOMO-2	-5.303	0	100
HOMO-3	-5.311	0	100
HOMO-4	-5.904	4	96

Table S4. DFT calculated frontier orbital energies and partial contributions of **4a-Me** in the state T_1 geometry resulting from Mulliken population analysis.

Orbitals	**Energy, eV**	**Contributions, %**	
		Terephthalonitrile	**Methoxyphenyl substituted carbazoles**
LUMO+4	-1.925	0	100
LUMO+3	-2.248	2	98
LUMO+2	-2.285	1	99
LUMO+1	-2.849	78	22
LUMO	-4.027	93	7
HOMO	-5.052	2	98
HOMO-1	-5.140	3	97
HOMO-2	-5.351	2	98
HOMO-3	-5.370	2	98
HOMO-4	-5.388	1	99

Table S5. DFT calculated frontier orbital energies and partial contributions of **4b-Me** in the state T_1 geometry resulting from Mulliken population analysis.

Orbitals	Energy, eV	Contributions, %	
		Terephthalonitrile	Methoxyphenyl substituted carbazoles
LUMO+4	-1.816	1	99
LUMO+3	-2.288	3	97
LUMO+2	-2.319	1	99
LUMO+1	-2.892	79	21
LUMO	-4.027	93	7
HOMO	-4.903	2	98
HOMO-1	-4.959	2	98
HOMO-2	-5.107	0	100
HOMO-3	-5.123	0	100
HOMO-4	-5.170	1	99

Table S6. TD-DFT calculated lowest triplet and singlet states of **IrIr'** in the T$_1$ state geometry.

State, energy (eV)	*f* (oscillator strength)	Contributing transition coefficients*	Character**
triplets			
T$_1$, 1.514	(triplet)	HOMO→LUMO (0.70)	LC^{CN-CN}/ M$^{Ir1/Ir2}$L^{CN-CN}CT
T$_2$, 2.124	(triplet)	HOMO–2→LUMO (0.70)	M$^{Ir1/Ir2}$L^{CN-CN}CT/L$^{Cl1/Cl2}$L^{CN-CN}CT/ LC^{CN-CN}
T$_3$, 2.140	(triplet)	HOMO–1→LUMO (0.70)	M$^{Ir1/Ir2}$L^{CN-CN}CT/L$^{Cl1/Cl2}$L^{CN-CN}CT/ L$^{NCN1/NCN2}$L^{CN-CN}CT
T$_4$, 2.182	(triplet)	HOMO–3→LUMO (0.70)	LC^{CN-CN} /M$^{Ir1/Ir2}$L^{CN-CN}CT/ L$^{Cl1/Cl2}$L^{CN-CN}CT
T$_5$, 2.344	(triplet)	HOMO→LUMO+1 (0.70)	L^{CN-CN}L$^{NCN1/NCN2}$ CT
singlets			
S$_1$, 2.048	0.2915	HOMO→LUMO (0.68) HOMO–4→LUMO (-0.15)	LC^{CN-CN}/ M$^{Ir1/Ir2}$L^{CN-CN}CT
S$_2$, 2.153	0.0000	HOMO–1→LUMO (0.70)	M$^{Ir1/Ir2}$L^{CN-CN}CT/L$^{Cl1/Cl2}$L^{CN-CN}CT/ L$^{NCN1/NCN2}$L^{CN-CN}CT
S$_3$, 2.194	0.0012	HOMO–3→LUMO (0.71)	LC^{CN-CN} /M$^{Ir1/Ir2}$L^{CN-CN}CT/ L$^{Cl1/Cl2}$L^{CN-CN}CT
S$_4$, 2.252	0.0000	HOMO–2→LUMO (0.70)	M$^{Ir1/Ir2}$L^{CN-CN}CT/L$^{Cl1/Cl2}$L^{CN-CN}CT/ LC^{CN-CN}
S$_5$, 2.359	0.0184	HOMO→LUMO+1 (0.71)	L^{CN-CN}L$^{NCN1/NCN2}$ CT

*Square of the coefficient multiplied by two gives percentage contribution of the transition to formation of the excited state.

**MLCT – Metal (M) to Ligand (L) Charge Transfer. LC-Ligand Centred. LLCT – Ligand-to-Ligand Charge Transfer.

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