Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information

Optimization of carbazole-pyrimidine linking pattern for achieving efficient TADF

Tomas Serevičius,*[a] Jelena Dodonova,[b] Rokas Skaisgiris,[a] Dovydas Banevičius,[a] Karolis Kazlauskas,[a] Saulius Juršėnas[a] and Sigitas Tumkevičius[b]

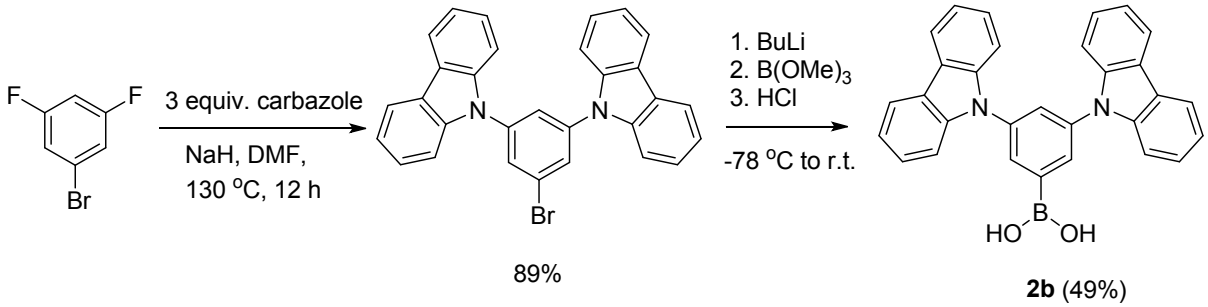
[a]Institute of Photonics and Nanotechnology, Vilnius University, Sauletekio 3, LT-10257 Vilnius, Lithuania.
[b]Institute of Chemistry Vilnius University, Naugarduko 24, LT-03225, Vilnius, Lithuania.
Corresponding author: E-mail: tomas.serevicius@tmi.vu.lt

Table of Contents

Synthesis and characterization data of compounds

Synthesis of (3,5-di(9*H*-carbazol-9-yl)phenyl)boronic acid (2b).

The required boronic acid **2b** was synthesized starting with 3,5-difluorobromobenzene by two step protocol according to scheme S1.

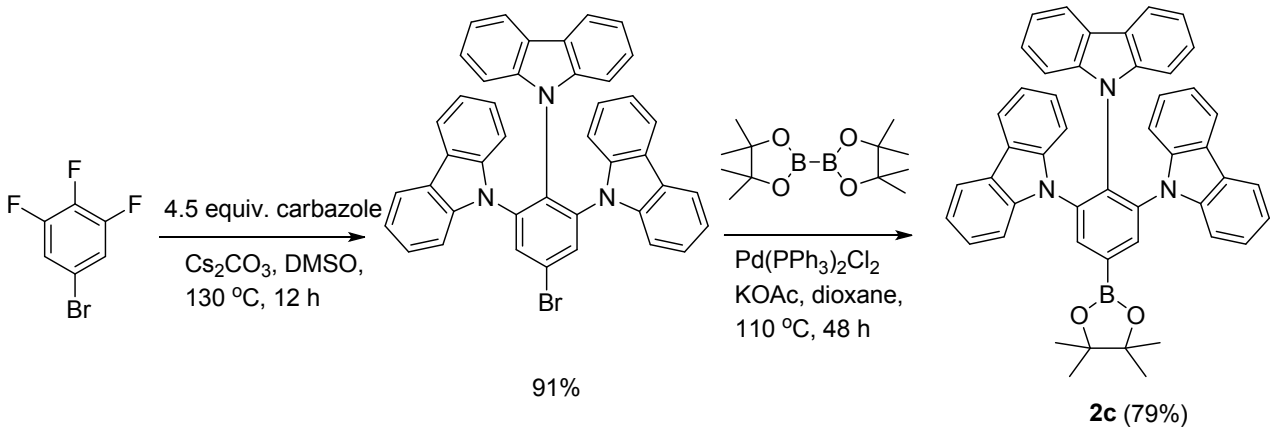


Scheme S1. Synthesis of [3,5-Di(9-carbazolyl)phenyl]boronic acid (**2b**).

9,9'-(5-Bromo-1,3-phenylene)bis(carbazole). To an anhydrous DMF solution (20 mL) containing sodium hydride (60% suspension in oil, 0.65 g, 16.9 mmol), carbazole (3 equiv., 2.6 g, 15.5 mmol) was slowly added. The mixture was stirred for 1 h at room temperature. After cooling in an ice bath, 3,5-difluorobromobenzene (0.6 mL, 5.2 mmol) was added dropwise. The solution mixture was then heated at 130 °C for 12 h. After cooling, an excess amount of ethanol-water mixture (10:1) was added and stirred, resulting in white precipitate that was filtered off (2.23 g, 89% yield). ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 8.19 (d, *J* = 8 Hz, 4H), 7.90 (d, *J* = 4 Hz, 2H), 7.83 (m, 1H), 7.60-7.57 (m, 4H), 7.52-7.48 (m, 4H), 7.39-7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.48, 140.3, 128.7, 126.4, 124.1, 123.4, 123.8, 120.8, 120.6, 109.6. NMR spectra of bis(carbazole) match with those described in ref.[1]

[3,5-Di(9-carbazolyl)phenyl]boronic acid (2b). To a solution of 9,9'-(5-bromo-1,3-phenylene)bis(9*H*-carbazole) (2.0 g, 4.1 mmol) in 50 mL of anhydrous tetrahydrofuran 2.5 M *n*-butyllithium solution in hexanes (1.5 equiv., 2.5 mL, 6.0 mmol) was added dropwise at −78 °C under argon atmosphere and vigorous stirring. After stirring for 1 h, trimethyl borate (3 equiv., 1.4 mL, 12.3 mmol) was added at the same temperature and allowed to warm to room temperature overnight under stirring. Then 1 M hydrochloric acid was added dropwise until an acidic solution was obtained. After stirring for 1 h, the reaction mixture was poured into water and extracted with chloroform (4×40 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The crude product was then purified by precipitating with petroleum ether to give boronic acid **2b** as a white solid (0.91 g, 49%) and used in cross-coupling reaction without additional purification.). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.20-8.18 (m, 4H), 8.10 (d, *J* = 4 Hz, 2H), 7.96-7.95 (m, 1H), 7.60-7.54 (m, 4H), 7.50-7.46 (m, 4H), 7.37-7.34 (m, 4H).

Synthesis of 9,9',9''-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,2,3-triyl)tris(9*H*-carbazole) (**2c**) was carried out starting with 3,4,5-trifluorobromobenzene in two steps according to scheme S2.



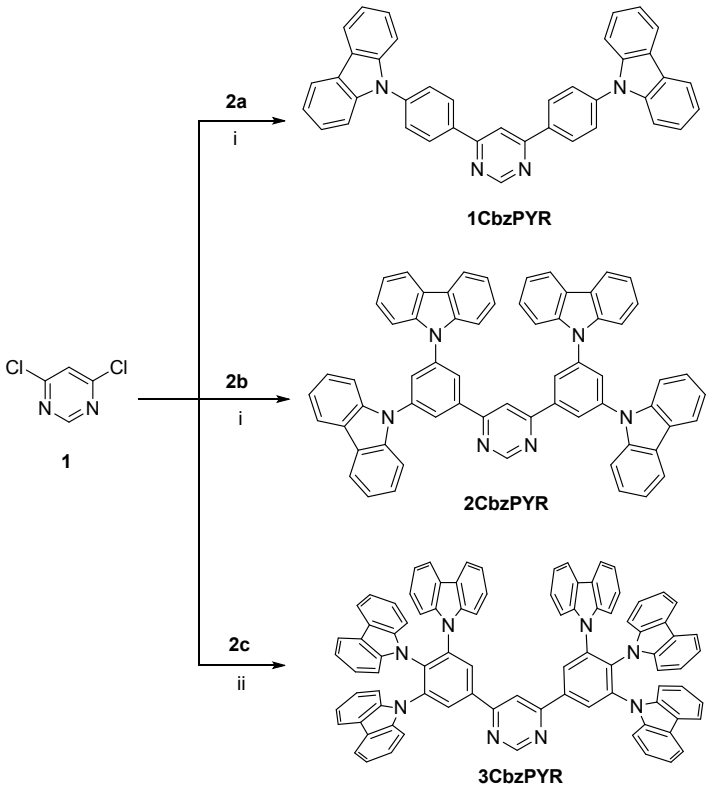
Scheme S2. Synthesis of 9,9',9''-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,2,3-triyl)tris(9*H*-carbazole) (**2c**).

9,9',9''-(5-bromobenzene-1,2,3-triyl)tris(carbazole). 1-Bromo-3,4,5-trifluorobenzene (0.1 g, 4.8 mmol) and 9*H*-carbazole (4.5 equiv., 0.36 g, 2.15 mmol) were dissolved in DMSO (10 mL) and Cs_2CO_3 (15 equiv., 2.34 g, 7.2 mmol) was added. The mixture was heated at 50-60°C for 72 h. After cooling to RT, excess amount of EtOH/H_2O (10:1) was added and stirred, resulting in white precipitate that was filtered off, washed with diethyl ether (20 ml) and used without further purification (0.28 g, 90.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (s, 2H), 7.82-7.78 (m, 4H), 7.40-7.38 (m, 2H), 7.27-7.23 (m, 4H), 7.11-7.04 (m, 8H), 6.96-6.94 (m, 2H), 6.82-6.78 (m, 2H), 6.71-6.6 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.6, 138.4, 138.1, 132.6, 125.8, 125.5, 124.6, 123.7, 123.5, 121.9, 120.4, 119.99, 119.92, 119.39, 109.8, 109.7. NMR spectra of tris(carbazole) match with those described in ref.[2]

9,9',9''-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,2,3-triyl)tris(9*H*-carbazole) (2c). 9,9',9''-(5-Bromobenzene-1,2,3-triyl)tris(9*H*-carbazole) (0.65 g, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol, 10 mol %), bis(pinacolato)diboron (1.05 equiv., 0.27 g, 1.05 mmol), KOAc (1.2 equiv., 0.12 g, 1.2 mmol) and dioxane (5 mL) were placed in a screw-cap vial equipped with a magnetic stir bar. The vial was purged with argon and the reaction mixture was stirred vigorously at 110 °C for 48 h under argon atmosphere. After completion of the reaction, water (20 mL) was added and the aqueous solution was extracted with chloroform (4×20 mL). The combined extract was dried with anhydrous Na_2SO_4, filtered and chloroform was removed by distillation under reduced pressure. Residue was purified by column chromatography using chloroform:petroleum ether (1:2) as an eluent to give compound **2c** as a white solid (0.55 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.37 (s, 2H), 7.81-7.79 (m, 4H), 7.39-7.37 (m, 2H), 7.26-7.24 (m, 4H), 7.08-7.04 (m, 8H), 7.02-6.99 (m, 2H), 6.78-6.77 (m, 2H), 6.69-6.6 (m, 2H), 1.42 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.97, 138.4, 136.8, 135.9, 134.3, 125.3, 124.5, 123.51, 123.5, 119.92, 119.86, 119.7, 119.3, 110.1, 109.9, 84.7, 24.98. HRMS-ESI: m/z calcd. for $[M+H]^+$ ($C_{48}H_{38}BN_3O_2$): 700.3129, found: 700.3136. NMR spectra of compound **2c** match with those described in ref.[2]

Synthesis of 1CbzPYR, 2CbzPYR and 3CbzPYR.

Emitters **1CbzPYR**, **2CbzPYR** and **3CbzPYR** were synthesized by the Suzuki-Miyaura cross-coupling reaction of 4,6-dichloropyrimidine (1) with the corresponding boronic acids (**2a, 2b**) or ester (**3c**) according to scheme S3.



Scheme S3. *Reagents and conditions*: i) boronic acid (**2a** or **2b**) (2.2 equiv.), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), aq. Na_2CO_3 (3.1 equiv.), glyme, 90 ºC, 24 h; ii) boronic ester (**2c**) (2.2 equiv.), $Pd(PPh_3)_4$ (10 mol%), aq. K_2CO_3 (15 equiv.), glyme, 80 °C, 24 h.

Synthesis of 4,6-bis[4-(9-carbazolyl)phenyl]pyrimidine (1CbzPYR) and 4,6-bis[3,5-di(9-carbazolyl)phenyl]pyrimidine (2CbzPYR). General procedure. 4,6-Dichloropyrimidine (**1**) (20 mg, 0.13 mmol), $Pd(OAc)_2$ (1.5 mg, 0.0065 mmol, 5 mol %), PPh_3 (3.5 mg, 0.013 mmol, 10 mol %), boronic acids **2a** or **2b** (2.2 equiv., 0.29 mmol), 1 mL of aqueous Na_2CO_3 (3.1 equiv., 44 mg, 0.4 mmol) and glyme (3 mL) were placed in a screw-cap vial equipped with a magnetic stir bar. The reaction mixture was stirred vigorously at 90 °C for 24 h under argon atmosphere. After completion of the reaction, water (20 mL) was added and the aqueous solution was extracted with chloroform (4×20 mL). The combined extracts were dried with anhydrous Na_2SO_4, filtered and chloroform was removed by distillation under reduced pressure. Residue was purified by column chromatography using chloroform:petroleum ether (1:2) as an eluent to give compounds **1CbzPYR** and **2CbzPYR.**

1CbzPYR: White solid, yield 80%, mp 313 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.47 (s, 1H), 8.48 (d, 4H, *J* = 8.5 Hz), 8.31 (s, 1H), 8.21 (d, 4H, *J* = 7.6 Hz), 7.84 (d, 4H, *J* = 8.5 Hz), 7.57 (d, 4H, *J* = 7.6 Hz), 7.49 (t, 4H, *J* = 7.6 Hz), 7.37 (t, 4H, *J* = 7.6 Hz). ^{13}C BMR (100 MHz, $CDCl_3$), δ (ppm): 164.0, 159.5, 140.49, 140.45, 135.7, 128.9, 127.3, 126.2, 123.8, 120.5, 120.46, 112.6, 109.8. HRMS-ESI: m/z calcd. for $[M+H]^+$ ($C_{40}H_{27}N_4$): 563.2230, found: 563.2234.

2CbzPYR: Yellow solid (28%), mp 250-252 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.44 (s, 1H), 8.53-8.52 (m, 4H), 8.25 (s, 1H), 8.19-8.17 (m, 8H), 8.02-8.03 (m, 2H), 7.62-7.56 (m, 8H), 7.49-7.43 (8H), 7.38-7.32 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.5, 159.7, 140.5, 140.41, 140.37, 127.7, 126.4, 124.6, 123.8, 120.6, 120.57, 113.2, 109.6. MS-MALDI-TOF: m/z calcd. for $[M+H]^+$ ($C_{64}H_{41}N_6$): 893.338, found: 893.939.

Synthesis of 4,6-bis[3,4,5-tri(9-carbazolyl)phenyl]pyrimidine (3CbzPYR). 4,6-Dichloropyrimidine (**1**) (20 mg, 0.13 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 10 mol %), compound **3c** (2.2 equiv., 200 mg, 0.29 mmol) and 2 mL of aqueous K_2CO_3 (15 equiv., 270 mg, 1.95 mmol) and glyme (3 mL) were placed in a screw-cap vial equipped with a magnetic stir bar. The reaction mixture was stirred vigorously at 80 °C for 24 h under argon atmosphere. After completion of the reaction, water (20 mL) was added and the aqueous solution was extracted with chloroform (4×20 mL). The combined extract was dried with anhydrous Na_2SO_4, filtered and chloroform was removed by distillation under reduced pressure. Residue was purified by column chromatography using chloroform:petroleum ether (1:2) as an eluent to give **3CbzPYR** as a yellowish solid (137 mg, 86%), mp 516 °C (DSC data). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.44 (s, 1H), 8.77 (s, 4H), 8.33 (s, 1H), 7.80-7.78 (m, 8H), 7.4-7.38 (m, 4H), 7.27-7.24 (m, 8H), 7.08-6.97 (m, 20H), 6.83-6.77 (m, 4H), 6.70-6.65 (m, H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): δ 162.9, 159.9, 139.7, 138.2, 138.1, 137.9, 134.1, 128.3, 125.5, 124.7, 123.7, 123.6, 120.3, 120.0, 119.99, 119.4, 112.9, 109.97, 109.7. MS-MALDI-TOF: m/z calcd. for $[M+H]^+$ ($C_{88}H_{55}N_8$): 1223.454, found: 1223.406.

References:

1. Y.-T. Lee, Y.-T. Chang, C.-L. Wu, J. Golder, C.-T. Chen, C.-T. Chen, *Molecules* **2016**, *21*, 1315-1325.
2. M. Godumala, J. Yoon, C. Lee, J.-E. Jeong, S. Park, H. Y. Woo, M. J. Cho, D. H. Choi, *Chem. Commun*. **2019**, *55*, 12952—12955.

^{1}H and ^{13}C NMR spectra of the synthesized compounds

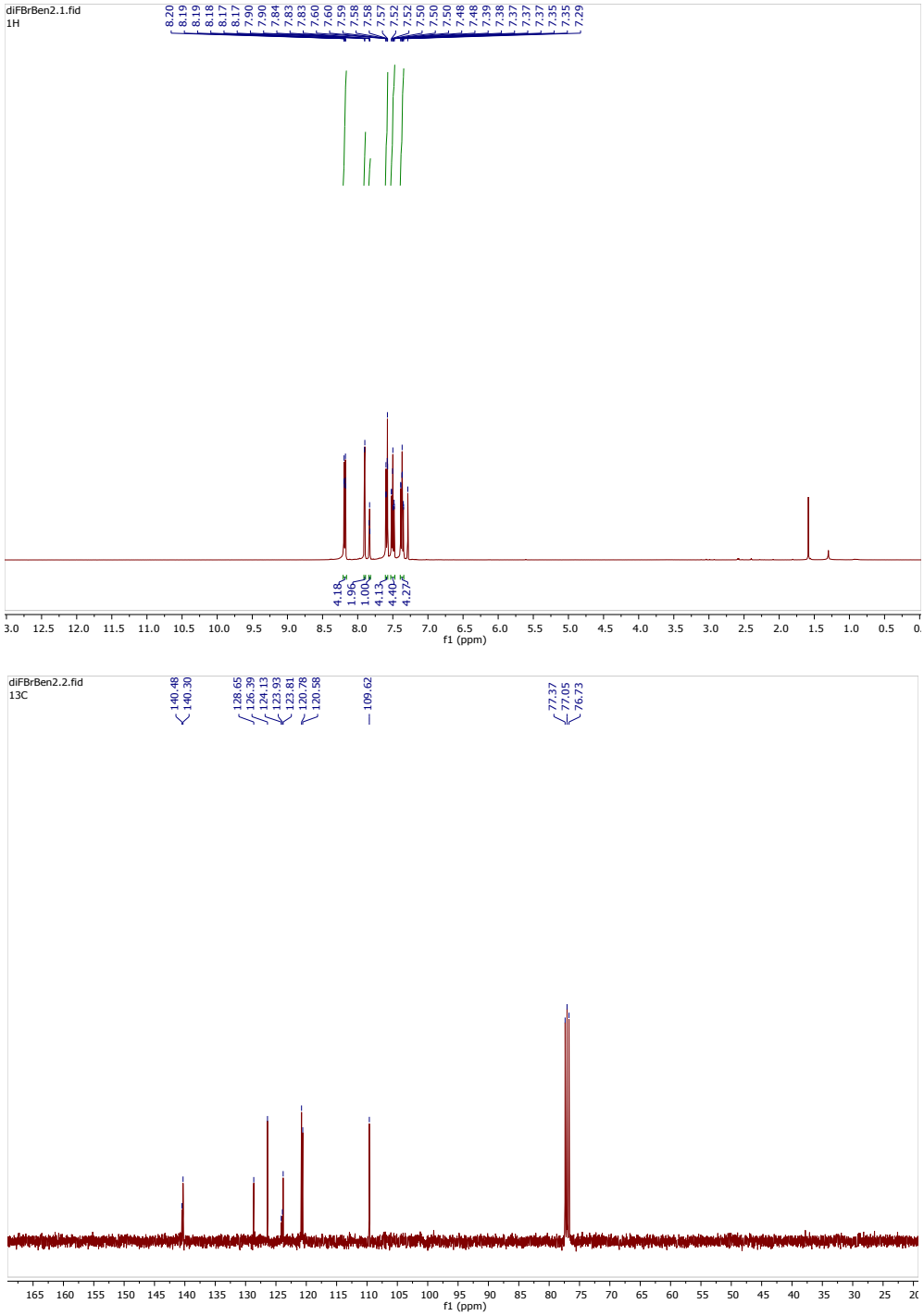


Fig. S1 ^{1}H and ^{13}C NMR spectra of 9,9'-(5-bromo-1,3-phenylene)bis(9*H*-carbazole).

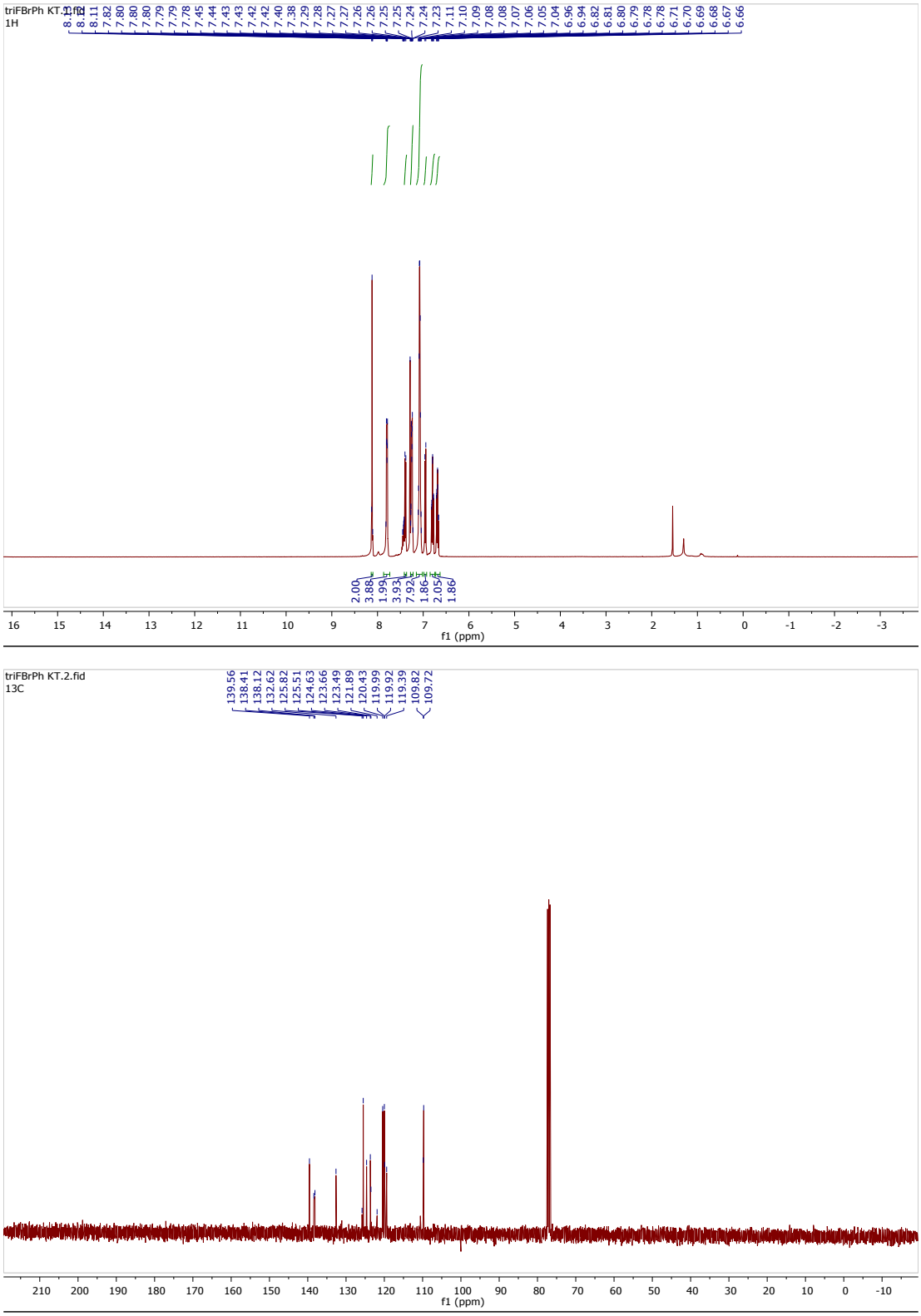


Fig. S2 ^{1}H and ^{13}C NMR spectra of 9,9',9''-(5-bromobenzene-1,2,3-triyl)tris(9*H*-carbazole)

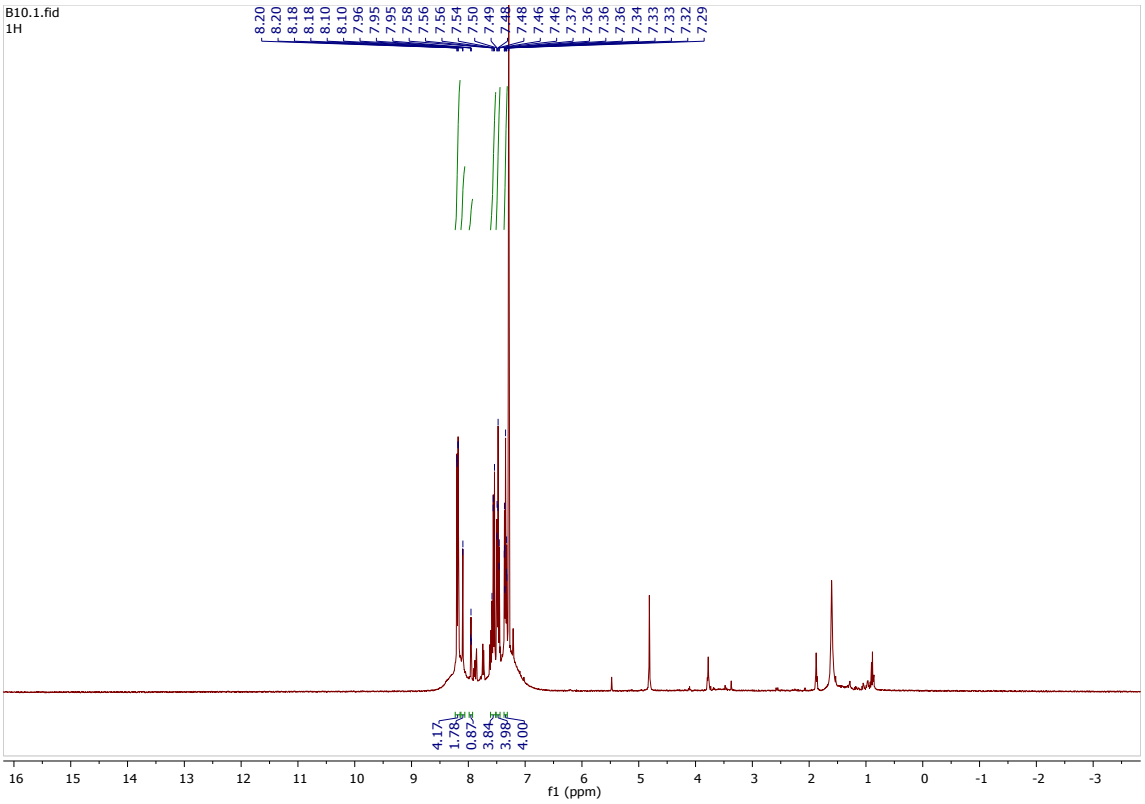


Fig. S3 ^{1}H NMR spectrum of (3,5-di(9*H*-carbazol-9-yl)phenyl)boronic acid (2b)

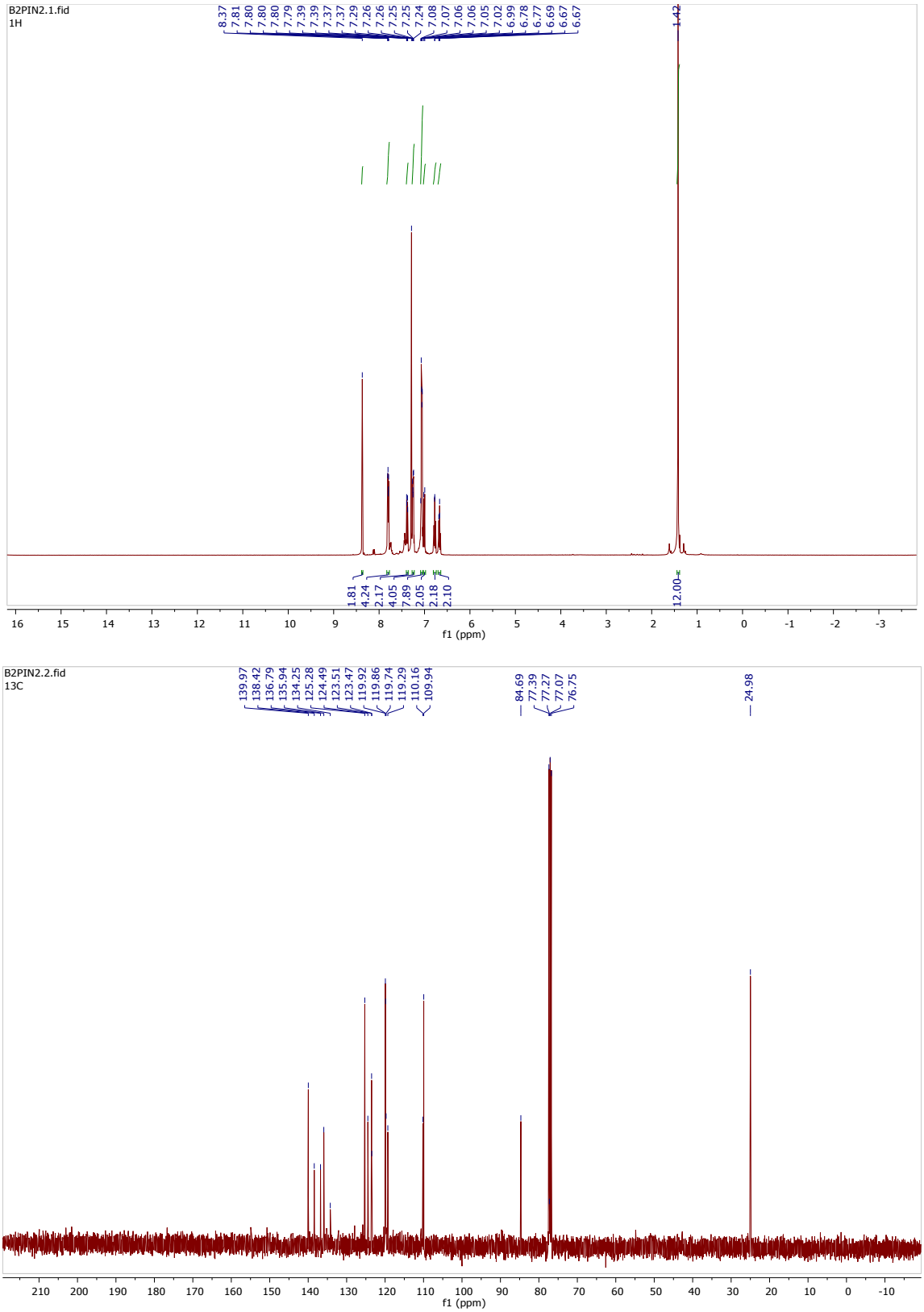


Fig. S4 ^{1}H and ^{13}C NMR spectra of 9,9',9''-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,2,3-triyl)tris(carbazole) (2c).

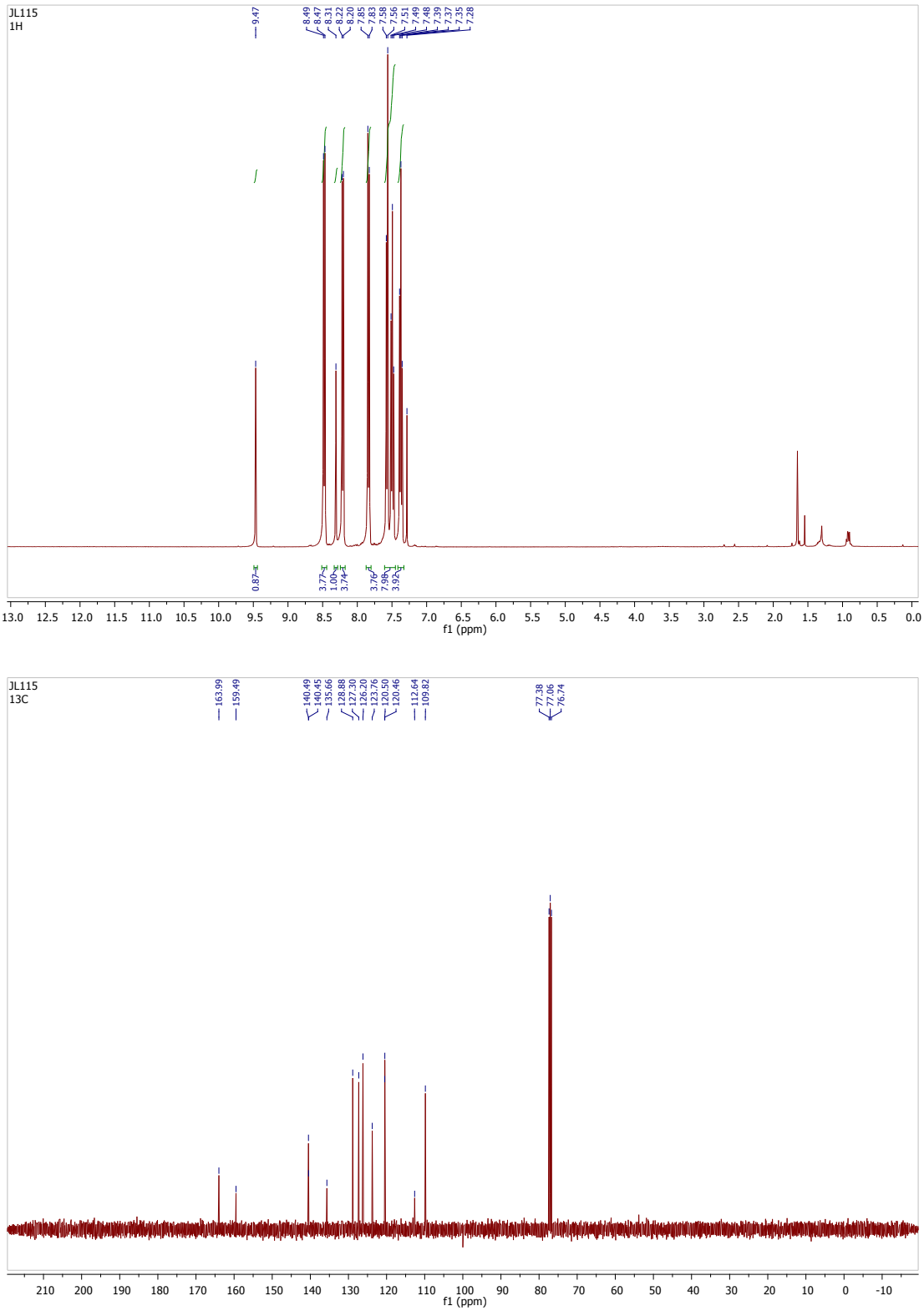


Fig. S5 ^{1}H and ^{13}C NMR spectrum of 4,6-bis[4-(9-carbazolyl)phenyl]pyrimidine (1CbzPYR).

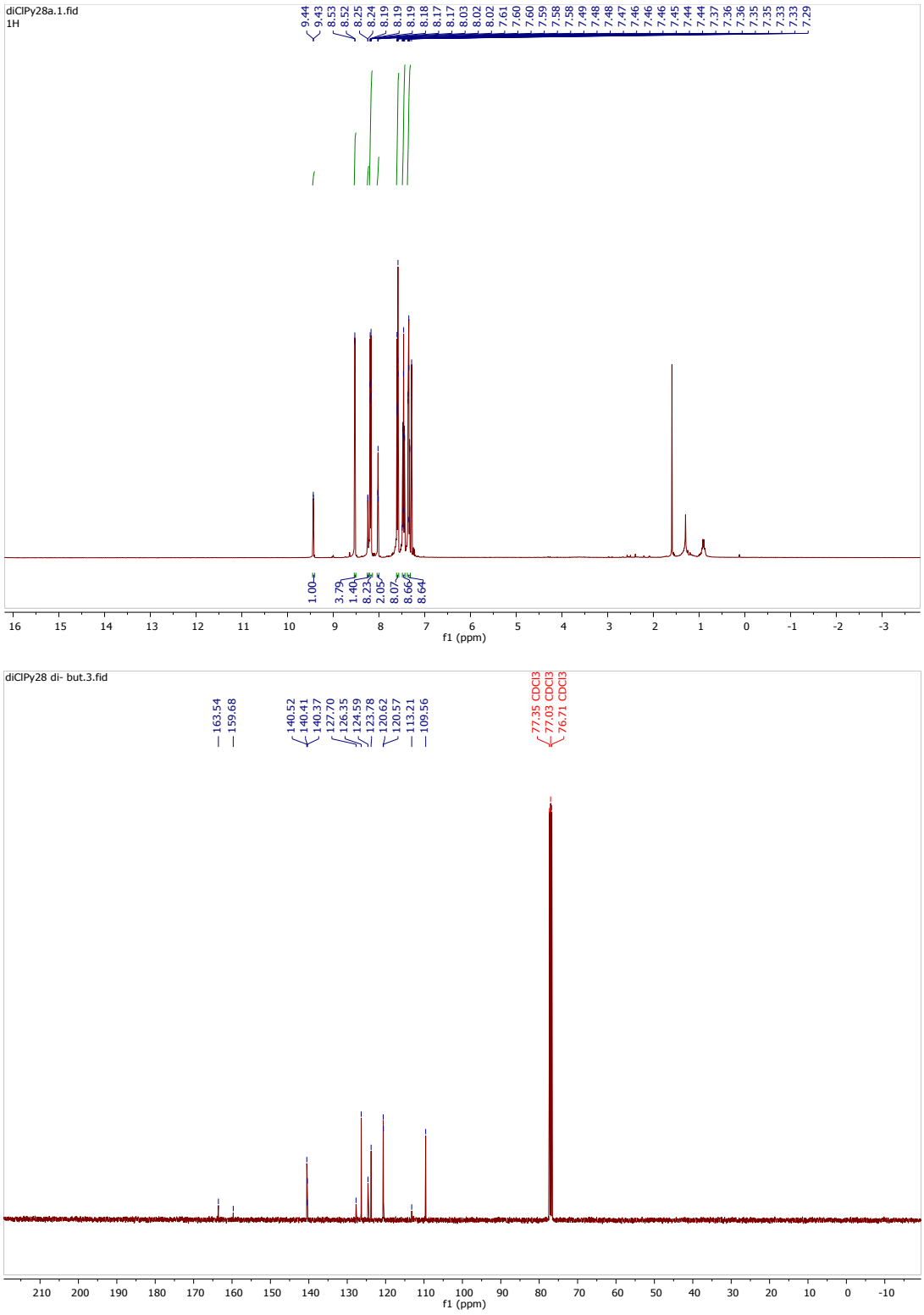


Fig. S6 ^{1}H and ^{13}C NMR spectra of 4,6-bis[3,5-di(9-carbazolyl)phenyl]pyrimidine (2CbzPYR).

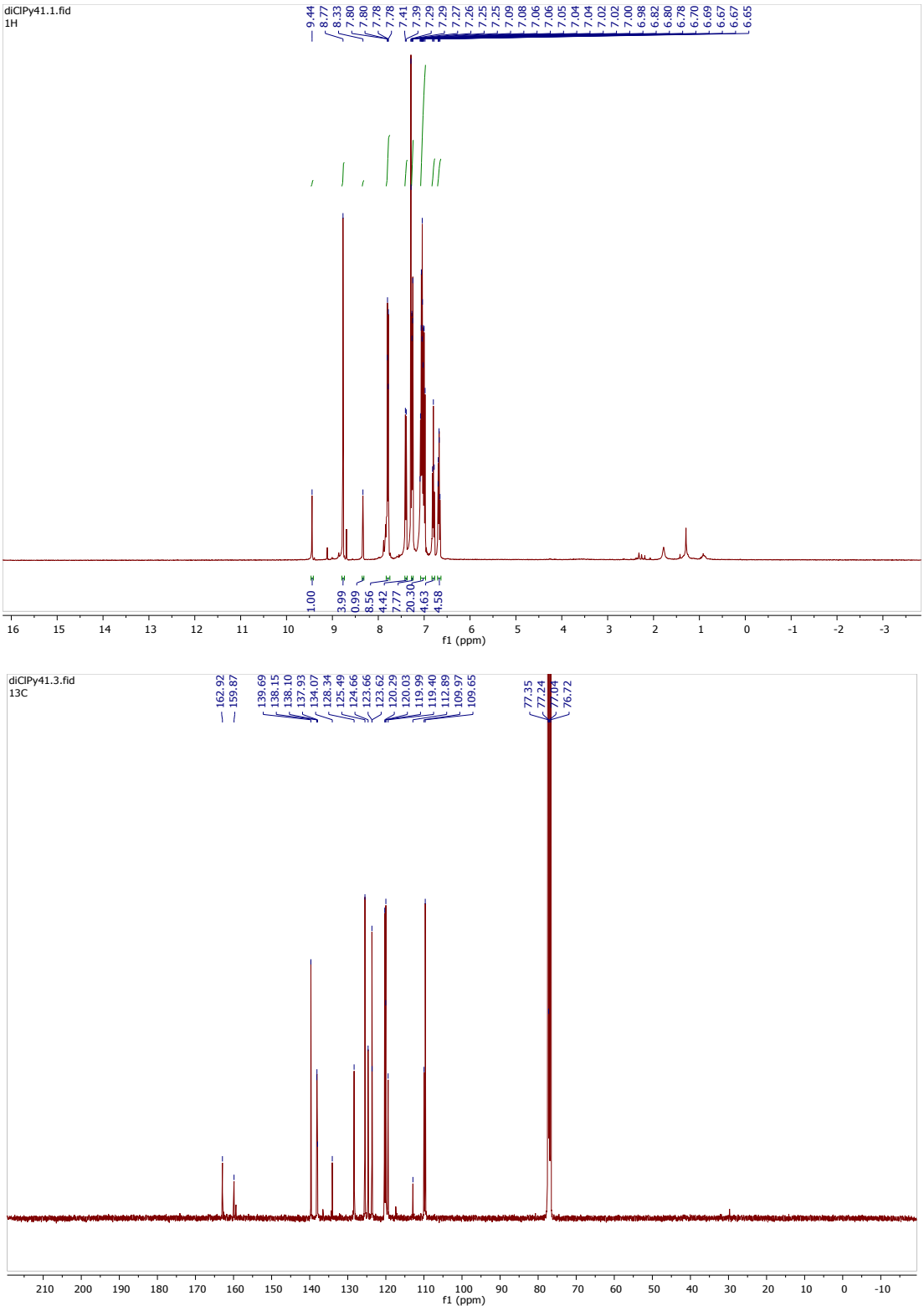


Fig. S7 ^{1}H and ^{13}C NMR spectra of 4,6-bis[3,4,5-tri(9-carbazolyl)phenyl]pyrimidine (3CbzPYR).

DFT calculations

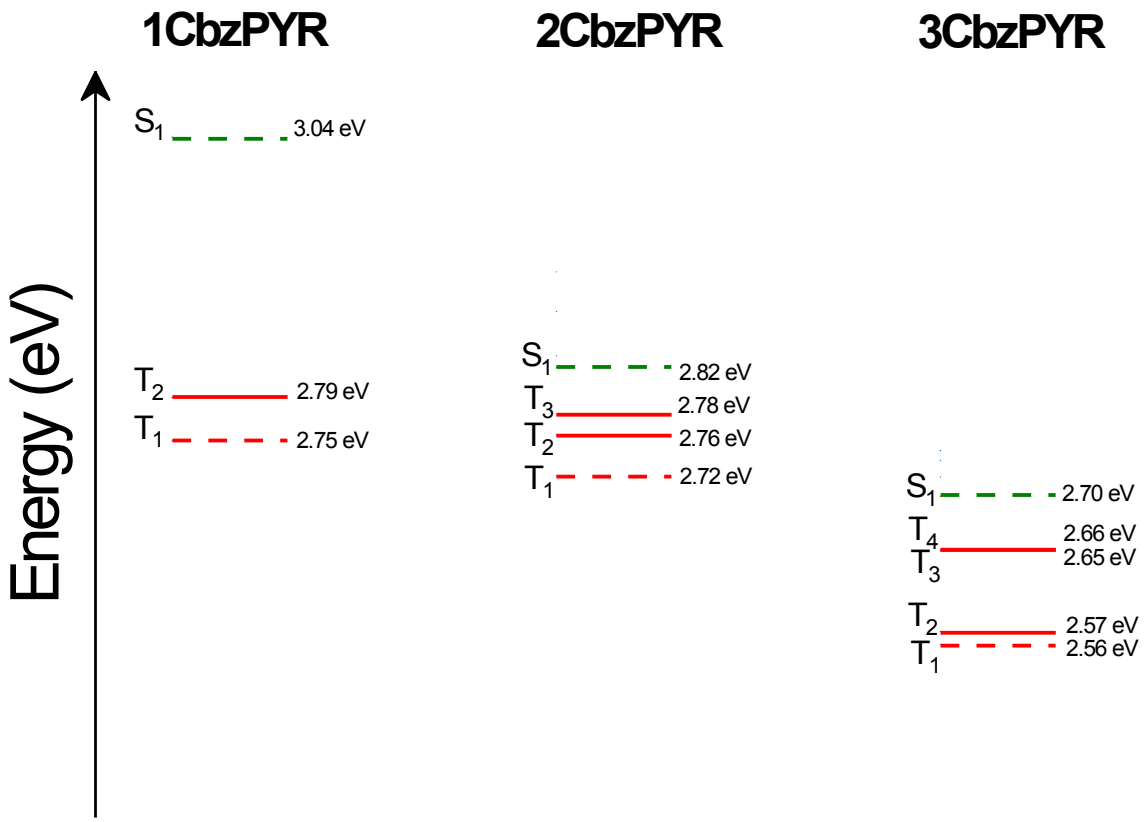


Fig. S8 Energy diagram of the lowest energy singlet and triplet states. S_1/T_1 states are shown with dashed lines. Calculations were performed at the B3LYP/6-31G(d) level including toluene solvation behaviour through PCM.

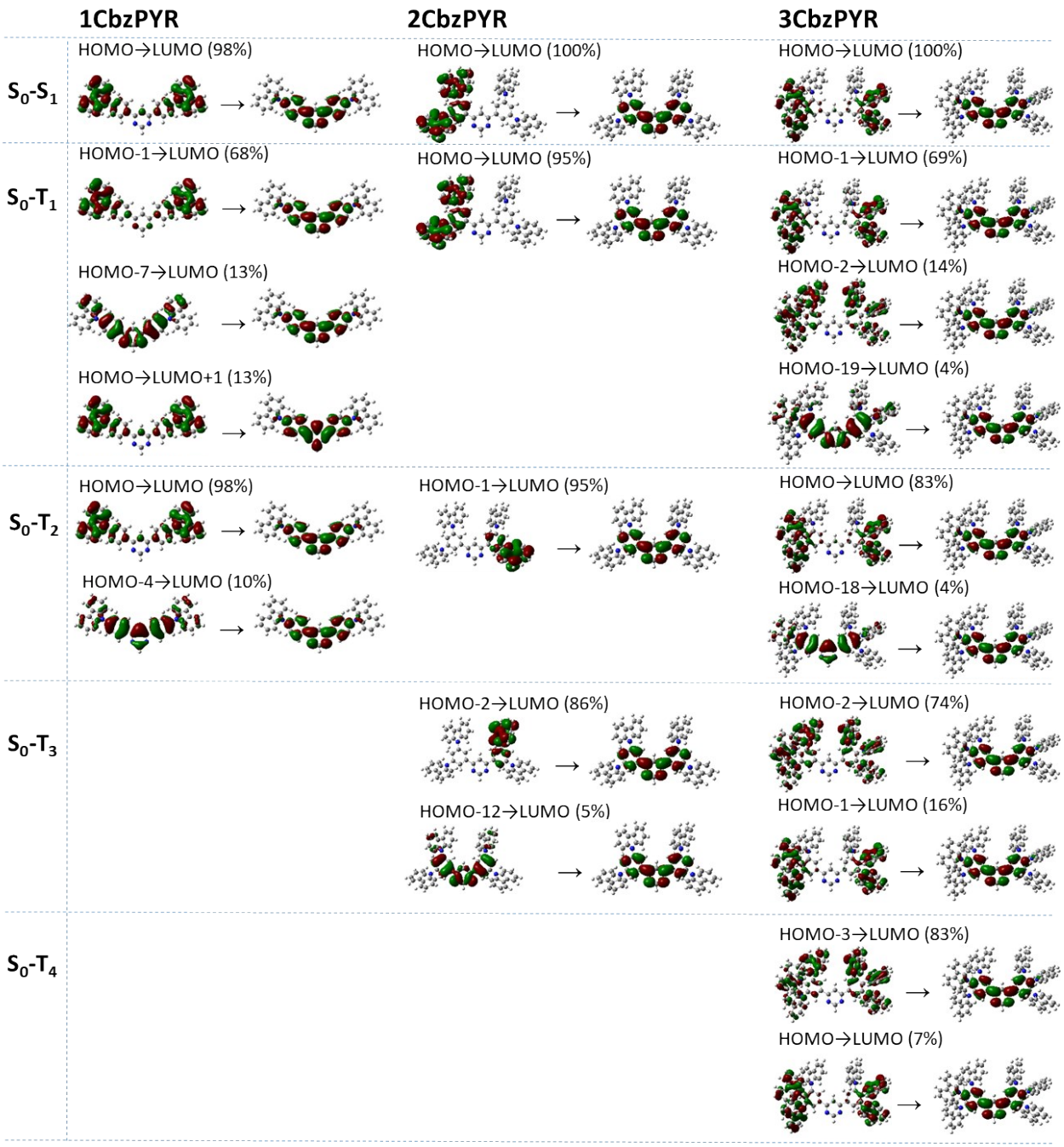


Fig.S9 Orbital composition for S_0-S_1 and S_0-T_n transitions with electron density distributions for the corresponding orbitals for carbazole-pyrimidine compounds. Left pictures represent HOMO-like orbitals, right pictures – LUMO-like orbitals. Probability for every transition is denoted. Calculations were performed at the B3LYP/6-31G(d) level including toluene solvation behaviour through PCM.

Extended photophysical properties

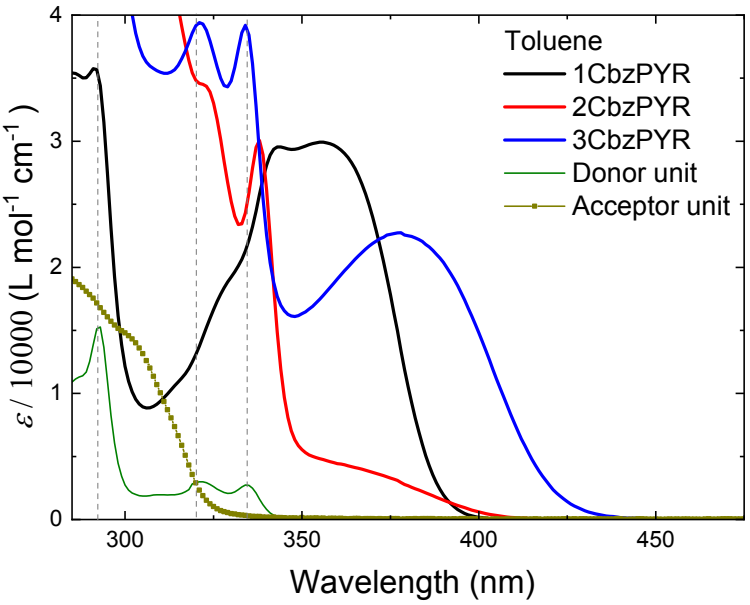


Fig. S10 Absorption spectra of compounds **1CbzPYR** (black line), **2CbzPYR** (red line), **3CbzPYR** (blue line) together with absorption spectra of sole donor (dark green line) and acceptor (dark yellow figures) units in toluene.

Table S1 Fluorescence peak and onset values of carbazole-pyrimidine compounds in toluene and 1 w% PMMA films.

	Toluene				**1 wt% PMMA**			
	Peak		*Onset*		*Peak*		*Onset*	
	λ_{PL} (nm)	E_{PL} (eV)	λ_{PL} (nm)	E_{PL} (eV)	λ_{PL} (nm)	E_{PL} (eV)	λ_{PL} (nm)	E_{PL} (eV)
1CbzPYR	408	3.04	380	3.26	408	3.04	375	3.30
2CbzPYR	442	2.80	402	3.08	440	2.82	391	3.17
3CbzPYR	464	2.67	417	2.97	446	2.78	401	3.09

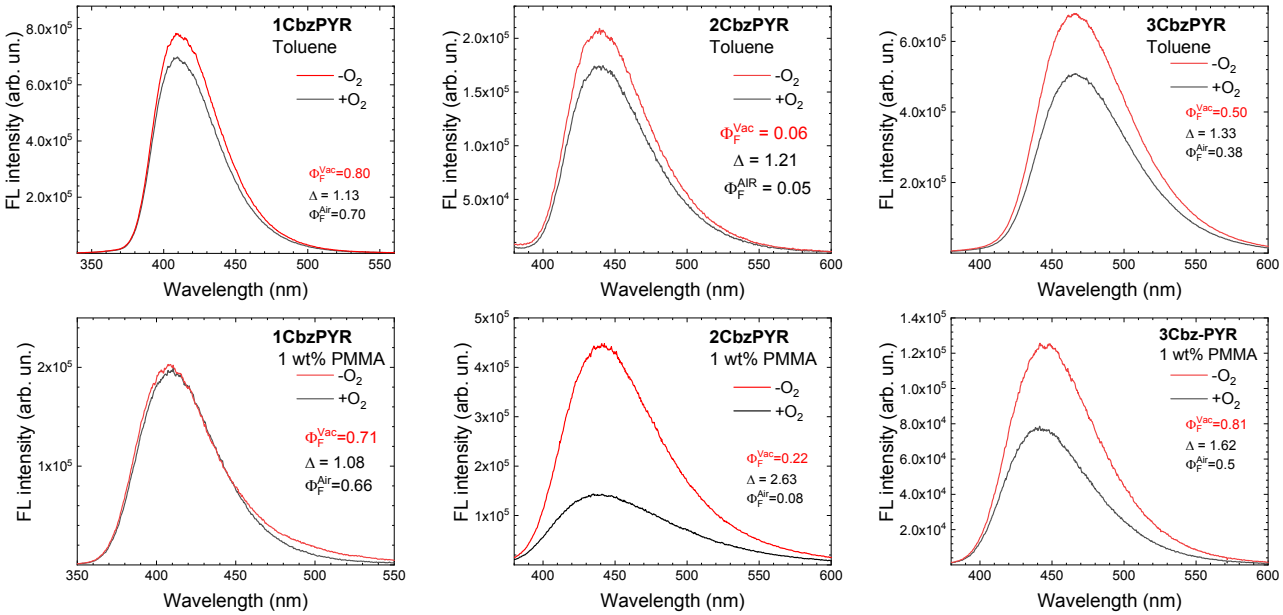


Fig. S11 Time-integrated fluorescence spectra of carbazole-pyrimidine compounds in toluene (upper pictures) and 1 wt% PMMA films (lower pictures) in $+O_2$ (black lines) and $-O_2$ (red lines) conditions. Please note, that Φ_F^{Air} contains a fraction of unquenched TADF, therefore is larger than the real value (see ref. 21 in the manuscript).

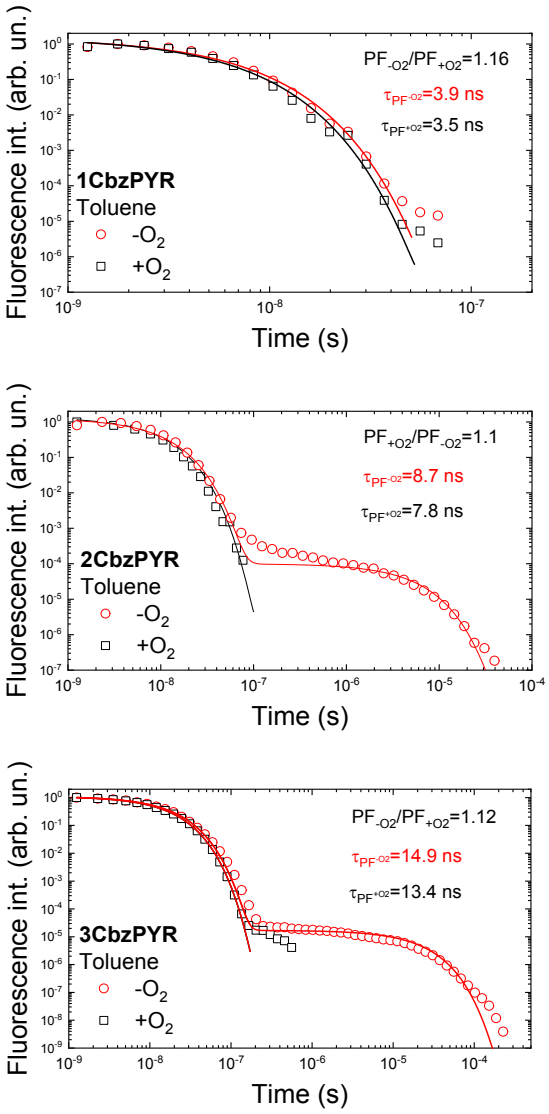


Fig. S12 Normalized fluorescence decay transients of carbazole-pyrimidine compounds in $+O_2$ (open squares) and $-O_2$ (open dots) toluene. Color lines are exponential/biexponential fits.

Table S2 Exponential fitting parameters of fluorescence decay transients of carbazole-pyrimidine compounds in toluene and PMMA surroundings. Exponential equation: $y = y_0 + A_1 e^{-(\frac{\tau}{\tau_{PF}})} + A_2 e^{-(\frac{\tau}{\tau_{DF}})}$. The second part of equation was used only for $-O_2$ toluene.

	$+O_2$ Toluene		$-O_2$ Toluene				$-O_2$ 1 wt% PMMA	
	τ_{PF} (ns)	A_1	τ_{PF} (ns)	A_1	τ_{DF} (μs)	A_2	τ_{PF} (ns)	A_1
1CbzPYR	3.5	1.560	3.9	1.495	-	-	4.1	1.119
2CbzPYR	7.8	1.350	8.7	1.249	4.5	1×10^{-4}	7.4	1.015
3CbzPYR	13.4	1.099	14.9	1.088	15	1.7×10^{-5}	15.5	0.984

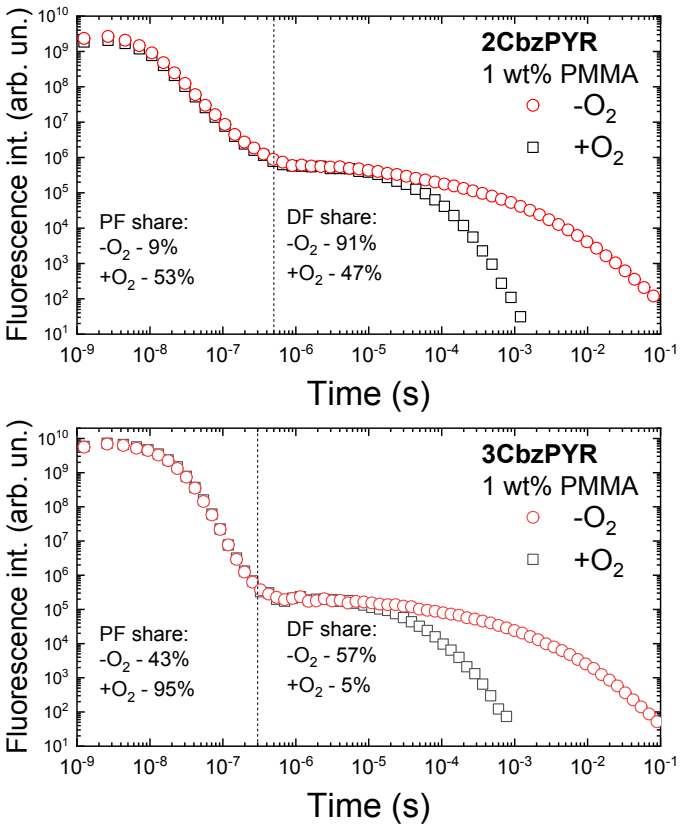


Fig. S13 Normalized fluorescence decay transients of 1 wt% PMMA films of carbazole-pyrimidine compounds **2CbzPYR** (upper picture) and **3CbzPYR** (lower picture) in $+O_2$ (open squares) and $-O_2$ (open dots) conditions.

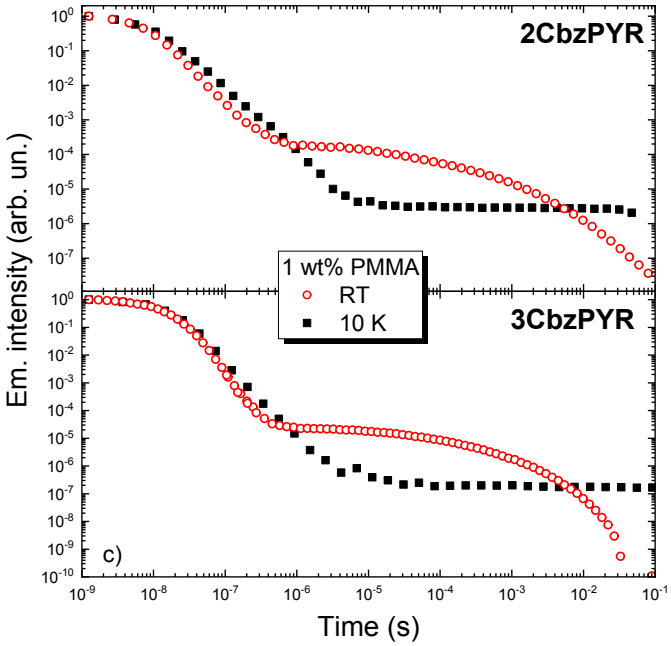


Fig. S14 Fluorescence decay transients of 1 wt% PMMA films of compounds **2CbzPYR** and **3CbzPYR** at room (open figures) and 10K temperature (closed figures).

Table S3 List of equations, used for calculation of TADF rates (according to ref. 25).

$k_{\mathrm{ISC}\rightarrow}$	$k_{PF}\Phi_{ISC}$
$k_{\mathrm{Risc}\rightarrow}$	$\Phi_{rISC}k_{TADF}\left(\frac{\Phi_{PF}+\Phi_{DF}}{\Phi_{PF}}\right)$
$\Phi_{\mathrm{ISC}\rightarrow}$	$1-\Phi_{PF}$
$\Phi_{\mathrm{rISC}\rightarrow}$	$\frac{\Phi_{DF}}{\Phi_{PL}\Phi_{ISC}}$
$k_{\mathrm{nr}^{\mathrm{T}}\rightarrow}$	$\frac{k_{rISC}}{\Phi_{rISC}}-k_{rISC}$

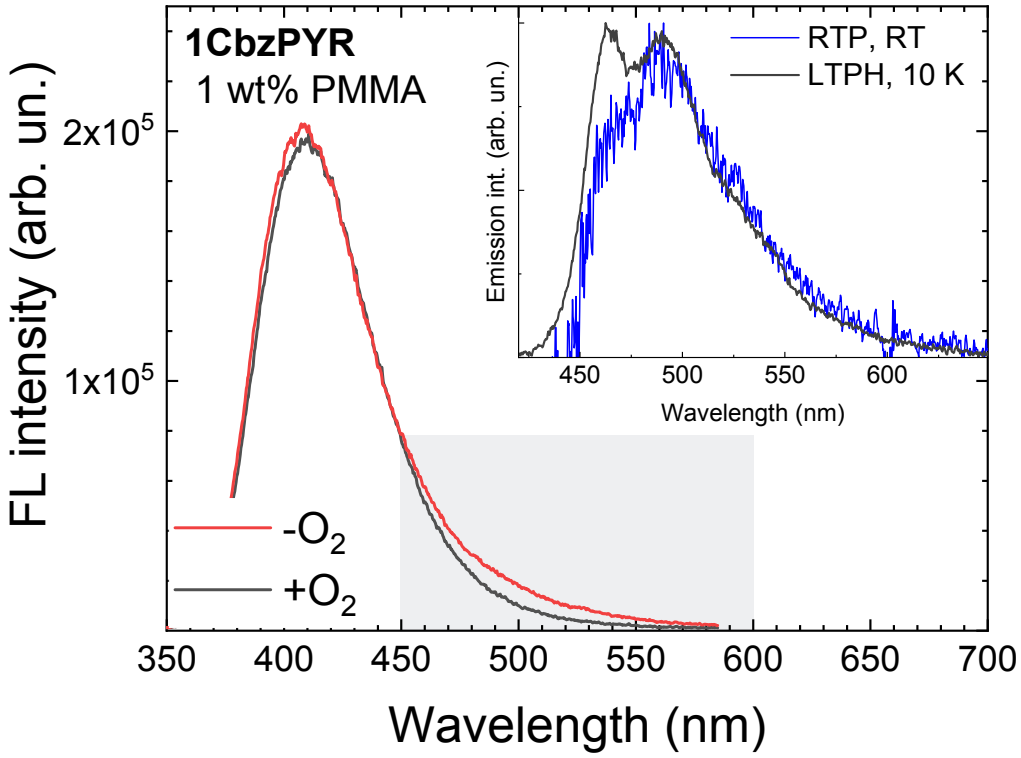


Fig. S15 Time-integrated emission spectra of 1 wt% PMMA film of **1CbzPYR** in $+O_2$ (black lines) and $-O_2$ (red lines) conditions. The grey rectangular marks the emergence of RTP in $-O_2$ conditions. The inset shows the comparison of low-temperature time-integrated phosphorescence (LTPH) spectrum (black line) and room-temperature time-integrated phosphorescence spectrum (RTP), obtained by subtracting the black spectrum ($+O_2$) from the red one ($-O_2$) shown in the main picture.

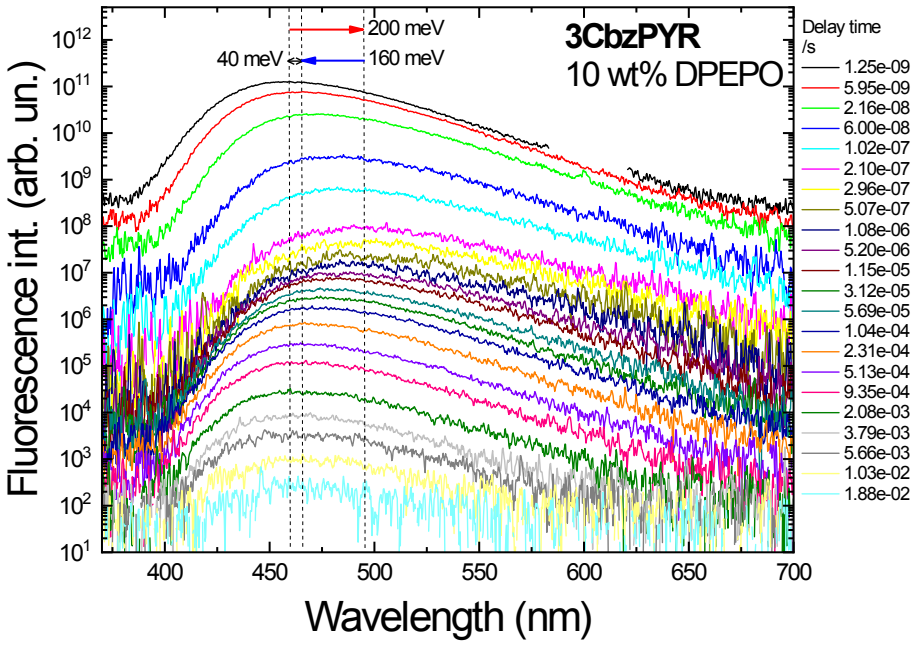


Fig. S16 Time-resolved fluorescence spectra of 10wt% DPEPO film of compound **3CbzPYR** in $-O_2$ conditions.

Thermal characterization

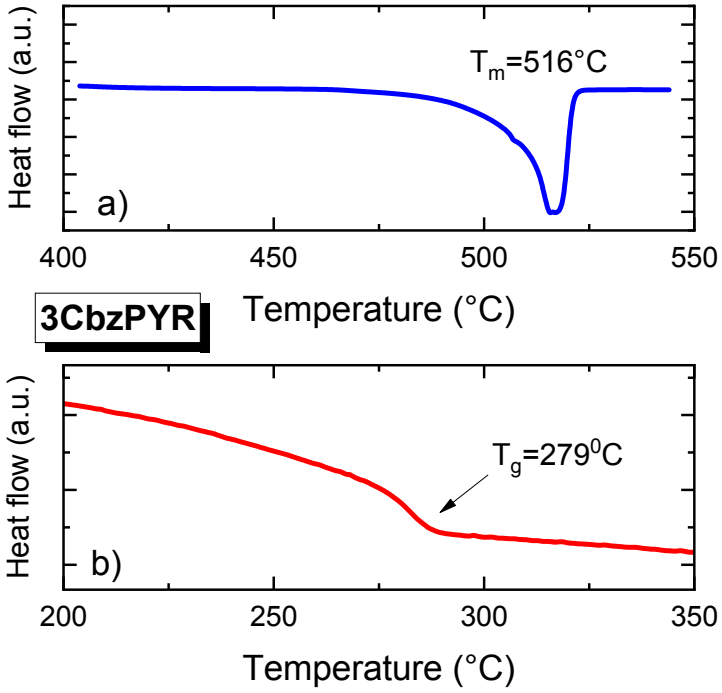


Fig. S17 DSC curves of compound **3CbzPYR**. First heating scan (a) and second heating scan (b).