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

Supporting Information for

Donor-Acceptor Materials Exhibiting Deep Blue Emission and Thermally Activated Delayed Fluorescence with Tris(triazolo)triazine

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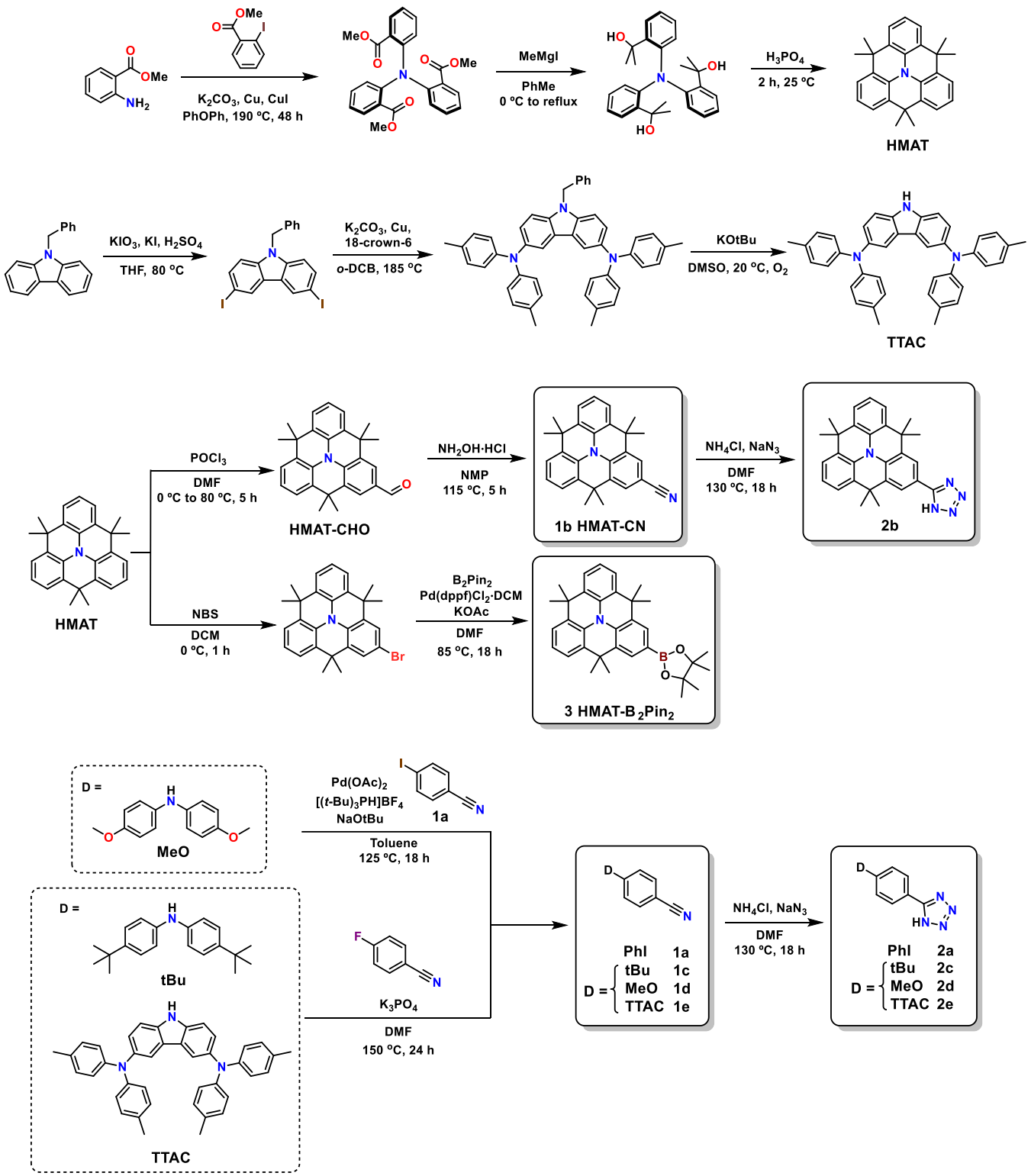


Scheme S1. Synthetic route for donor-appended aryl nitriles (**1a-e**), and subsequent conversion to tetrazoles (**2a-e**). In addition, synthetic routes to **HMAT**, **TTAC** and **3** are shown.

General Procedure for the Preparation of Aryl Nitriles via Nucleophilic Aromatic Substitution (1c, e). Aryl nitriles were prepared according to a modified literature procedure.[1,2] To a 100 mL round bottom flask equipped with a magnetic stir bar was added diarylamine (**tBu** or **TTAC**, 411 mg, 0.737 mmol, 1 eq.), 4-fluorobenzonitrile (268 mg, 2.211 mmol, 3 eq.), K_3PO_4 (783 g, 8.07 mmol, 3.685 eq.), and *N,N*-dimethylformamide (50 mL). The mixture was degassed with N_2 for 10 min before being heated to reflux using an oil bath for 24 hours under N_2 atmosphere. After the completion of reaction, the crude mixture was concentrated in *vacuo* to remove *N,N*-dimethylformamide. The viscous residue was suspended in water, followed by extractions with ethyl acetate (30 mL x 3). The combined organic fractions were washed with brine (20 mL x 1), followed by drying of the organic layer over $MgSO_4$, and concentration in vacuo. The crude product was purified by column chromatography over silica gel to afford aryl nitrile. Characterization data matched literature values.[1,2]

Procedure for the Preparation of Aryl Nitriles via Pd-catalyzed Cross Coupling (1d). Aryl nitriles were prepared according to a modified literature procedure.[3] To a 250 mL three neck round bottom flask equipped with a magnetic stir bar was added diarylamine (**MeO**, 1.5 g, 6.542 mmol, 1.0 eq.), 4-iodobenzonitrile (1.648 g, 7.196 mmol, 1.1 eq.), sodium butoxide (1.572 g, 16.36 mmol, 2.5 eq.), Pd $(OAc)_2$ (73 mg, 0.327 mmol, 0.05 eq), $[(t\text{-Bu})_3PH]BF_4$, (228 mg, 0.785 mmol, 0.12 eq) and toluene (125 mL). The reaction mixture was heated to reflux using an oil bath (125 ^oC) under N_2 atmosphere for 18 hours. After the completion of reaction, the crude mixture was concentrated in *vacuo* to remove toluene. The viscous residue was suspended in water, followed by extractions with ethyl acetate (30 mL x 3). The combined organic fractions were washed with brine (20 mL x 1), followed by drying of the organic layer over $MgSO_4$, and concentration in vacuo. The crude product was purified by column chromatography over silica gel to afford **1d**. Characterization data matched literature values.[3]

Photodestructive Quantum Yield Experiment: A mounted LED (ThorLabs 365 nm, 190 mW, model M365L2) was calibrated using chemical actinometry: a cuvette containing potassium ferrioxalate in an aqueous solution was stirred at room temperature and subsequently exposed to collimated radiation from a 365 nm excitation source for time intervals between 0 to 300 seconds. In concurrence with a standard curve for Fe^{2+}, the rate of incident photon radiation (I_0) on the experimental setup was determined using the equation below, where $N_{Fe}{}^{2+}$ is the number of Fe^{2+} ions formed in a given time interval (t):

$$I_0 = \frac{N_{Fe^{2+}}}{t[\Phi_{Fe^{2+}}]}$$

[Quantum yield of formation $\Phi_{Fe^{2+}} = 1.24$]

Concentrations of emitters **5-9** in toluene solutions were adjusted whereby their initial $A_{\lambda max}$ at t = 0 would lie within an absorbance range of 0.9 - 1.0 (Figure S25). The emitter was then exposed to a 365 nm LED, using the identical setup used for the actinometry calibration. The total light absorbed (I_a) for **5-9** was determined by the equation below:

$$I_a = \frac{I_0(1 - 10^{A_{365}})t}{V}$$

For time interval t, and the irradiated volume (V) of **5-9**, and the average absorbance at excitation wavelength A_{365}, I_a was summed over the course of the experiment. Plotting the diminishing $A_{\lambda max}$, as a function of I_a, yields a linear regression (Figure S25), with the equation as shown below:

$$y = \left[\frac{dA_{\lambda_{max}}}{dI_a}\right]x + b$$

Finally, the photodestructive quantum yield Φ_d (in units of 'molecules photon^{-1}') can be extracted from the above equation, in conjunction with Avogadro's number (N_A), the molar absorptivity of the sample (ε), and the path length of the cuvette (l) as shown below:

$$\Phi_d = \frac{N_A\left[-\frac{dA_{\lambda_{max}}}{dI_a}\right]}{\varepsilon l}$$

^{1}H and ^{13}C{^{1}H} NMR Spectroscopy (**α** = H_2O, **β** = Grease)

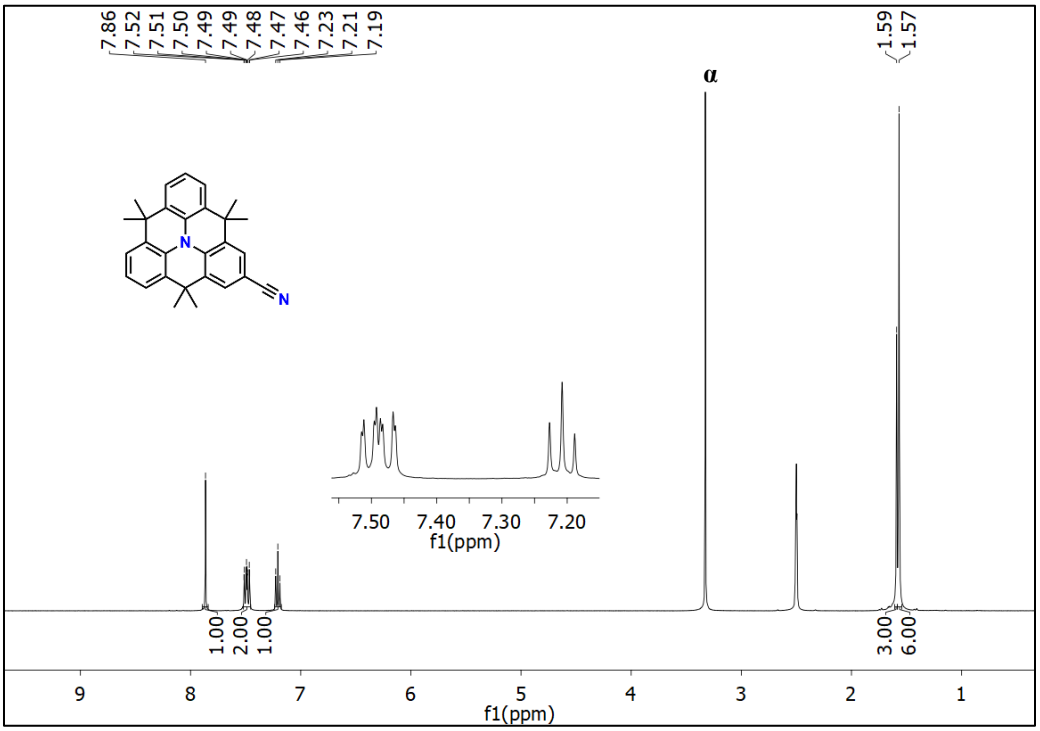


Figure S1. ^{1}H NMR (400 MHz) of **1b** in DMSO-d_6.

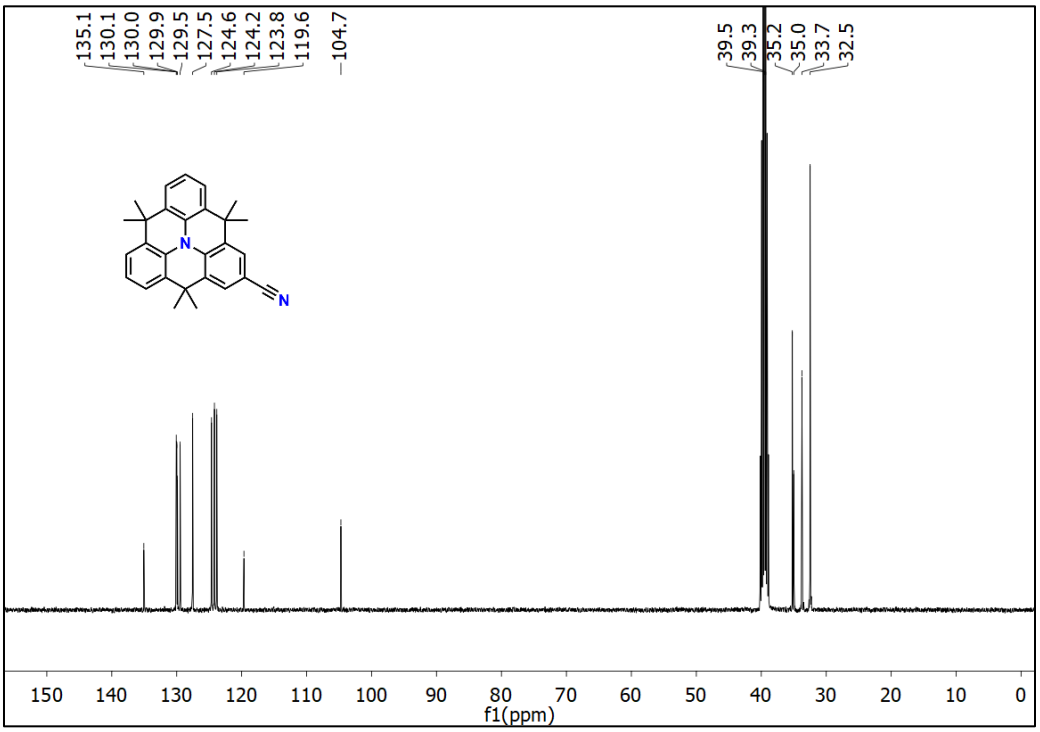


Figure S2. ^{13}C{^{1}H} NMR (101 MHz) of **1b** in DMSO-d_6.

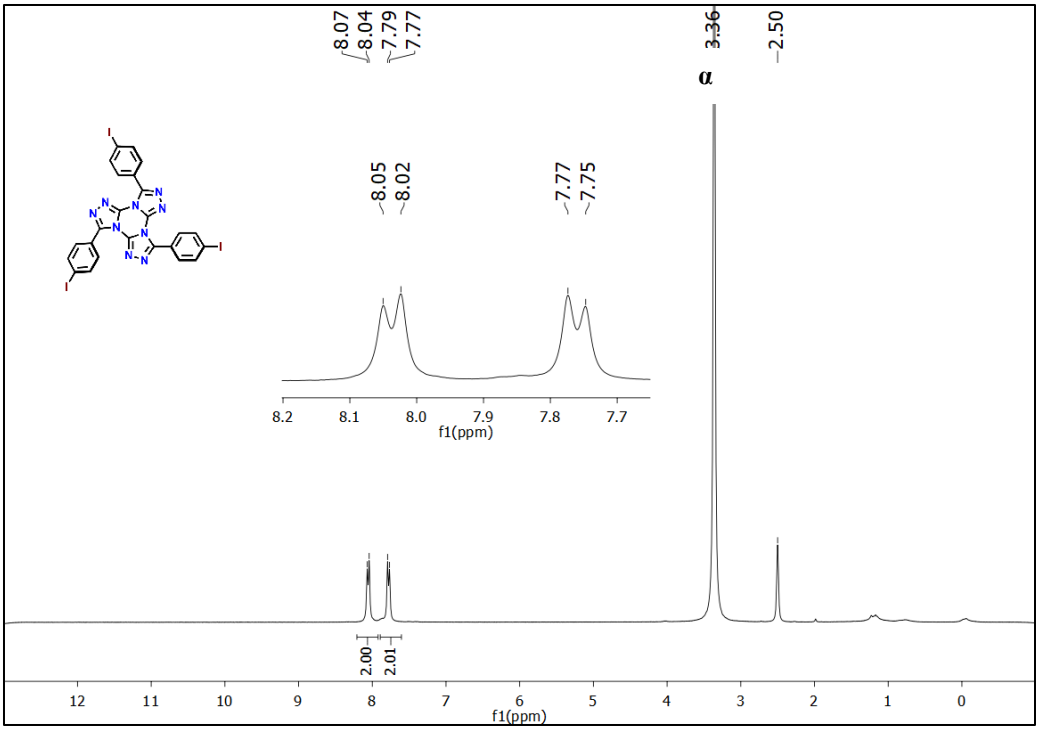


Figure S3. ^{1}H NMR (300 MHz) of **TTT-3PhI** (**4**) in DMSO-d_6.

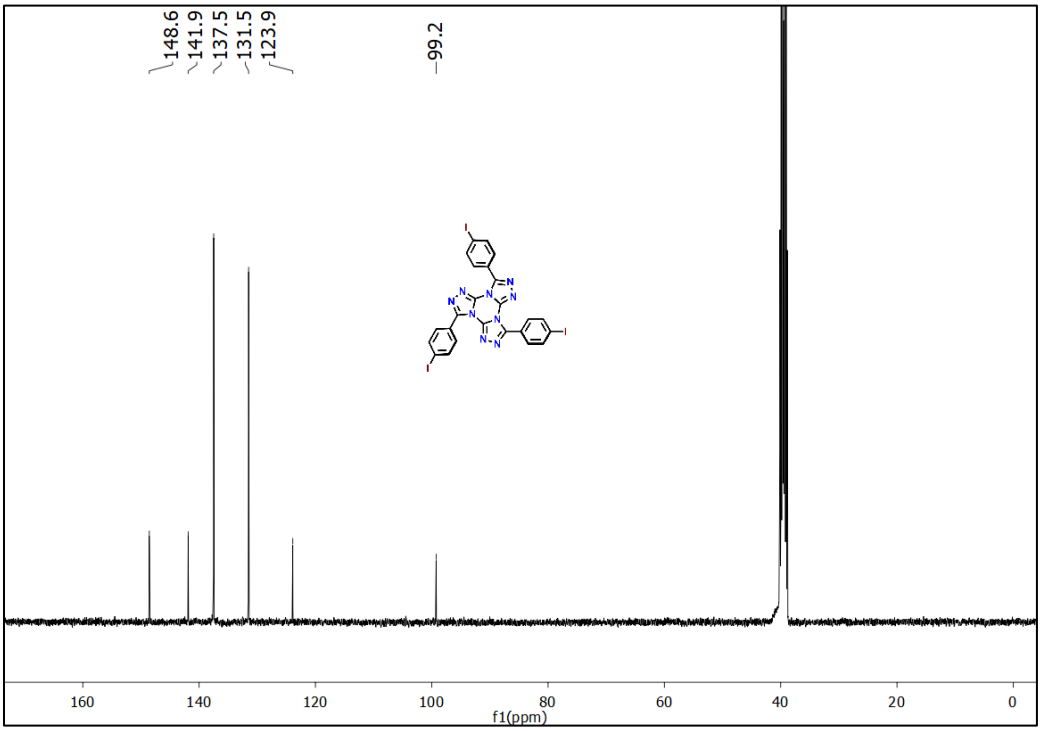


Figure S4. ^{13}C{^{1}H} NMR (101 MHz) of **TTT-3PhI** (**4**) in DMSO-d_6.

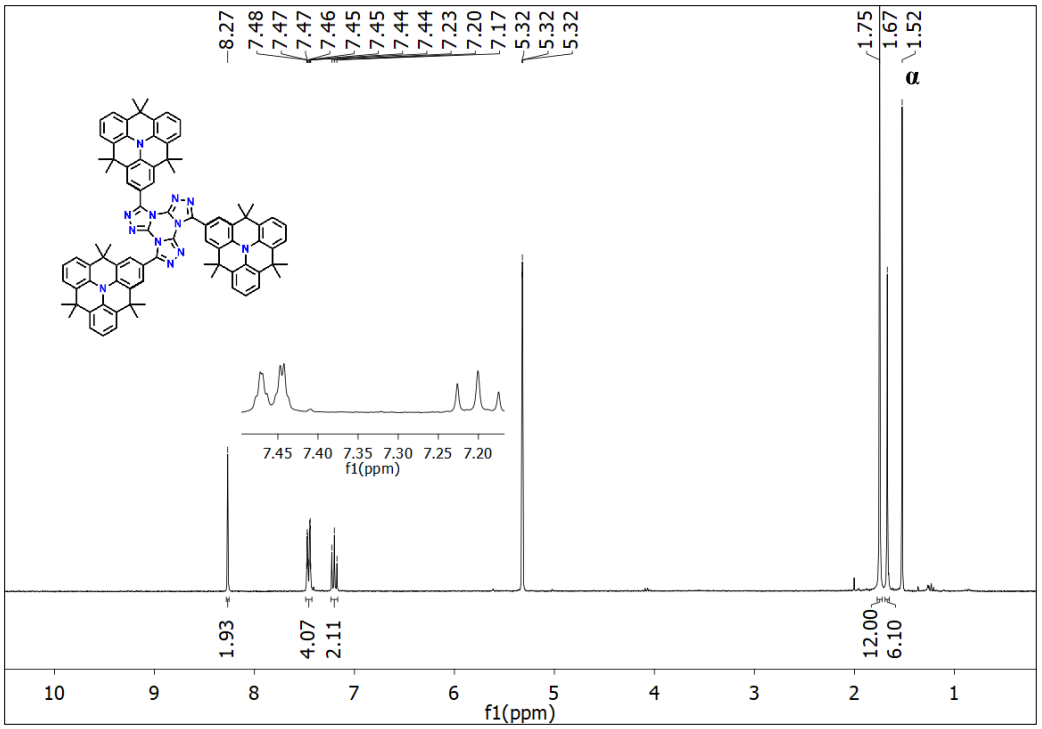


Figure S5. ^{1}H NMR (300 MHz) of **TTT-3HMAT** (**5**) in CD_2Cl_2.

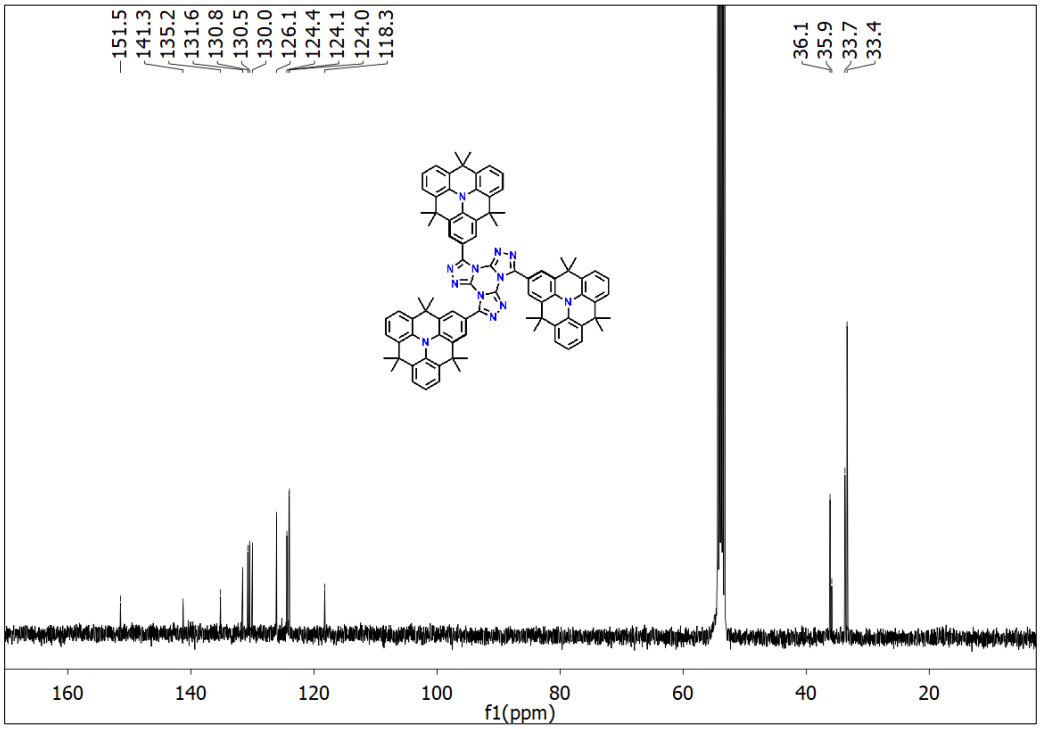


Figure S6. $^{13}C\{^{1}H\}$ NMR (101 MHz) of **TTT-3HMAT** (**5**) in CD_2Cl_2

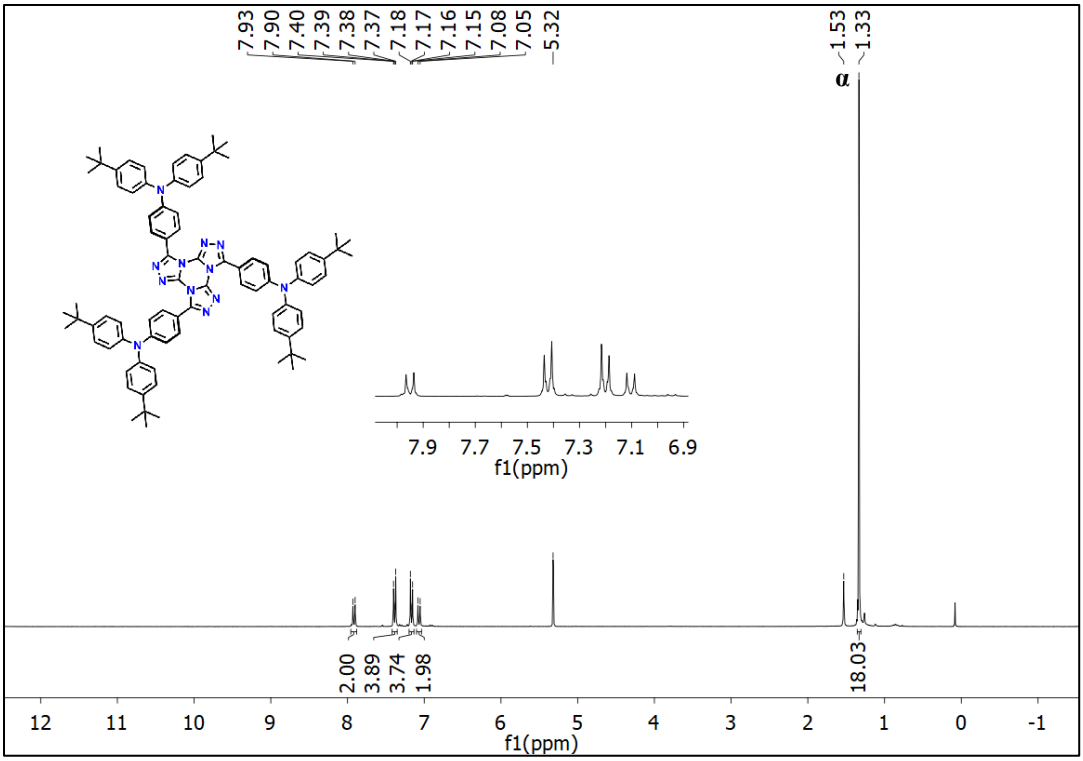


Figure S7. ^{1}H NMR (300 MHz) of **TTT-3tBu** (**6**) in CD_2Cl_2.

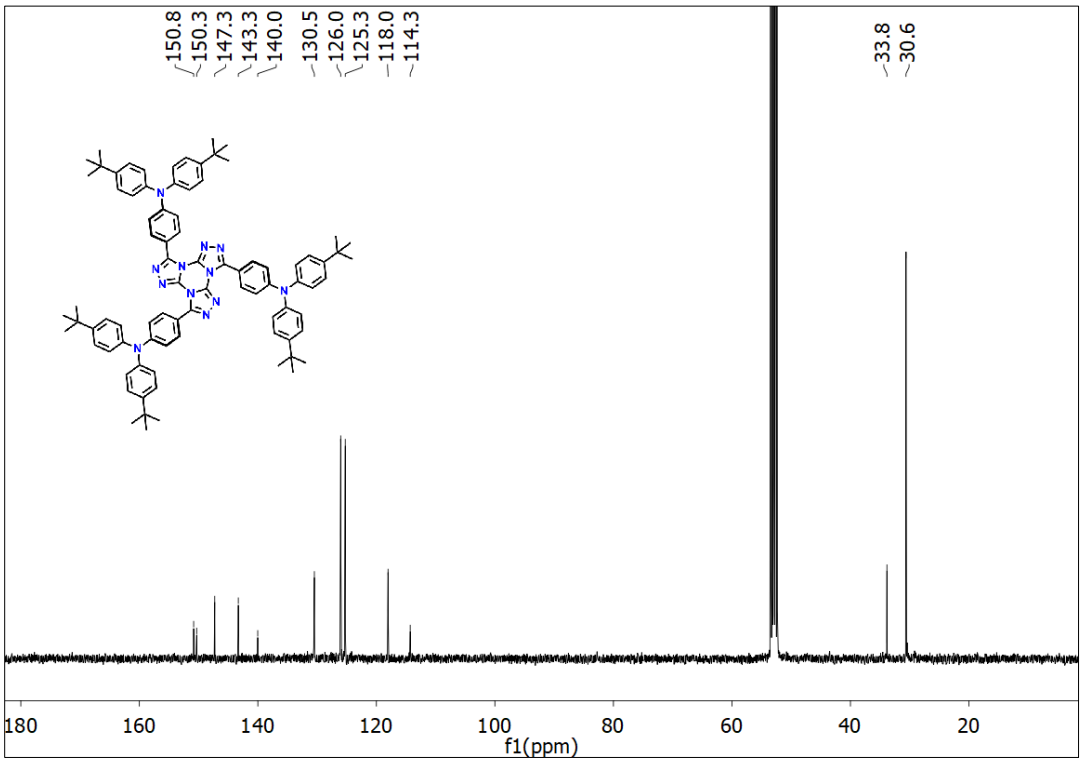


Figure S8. ^{13}C{^{1}H} NMR (101 MHz) of **TTT-3tBu** (**6**) in CD_2Cl_2.

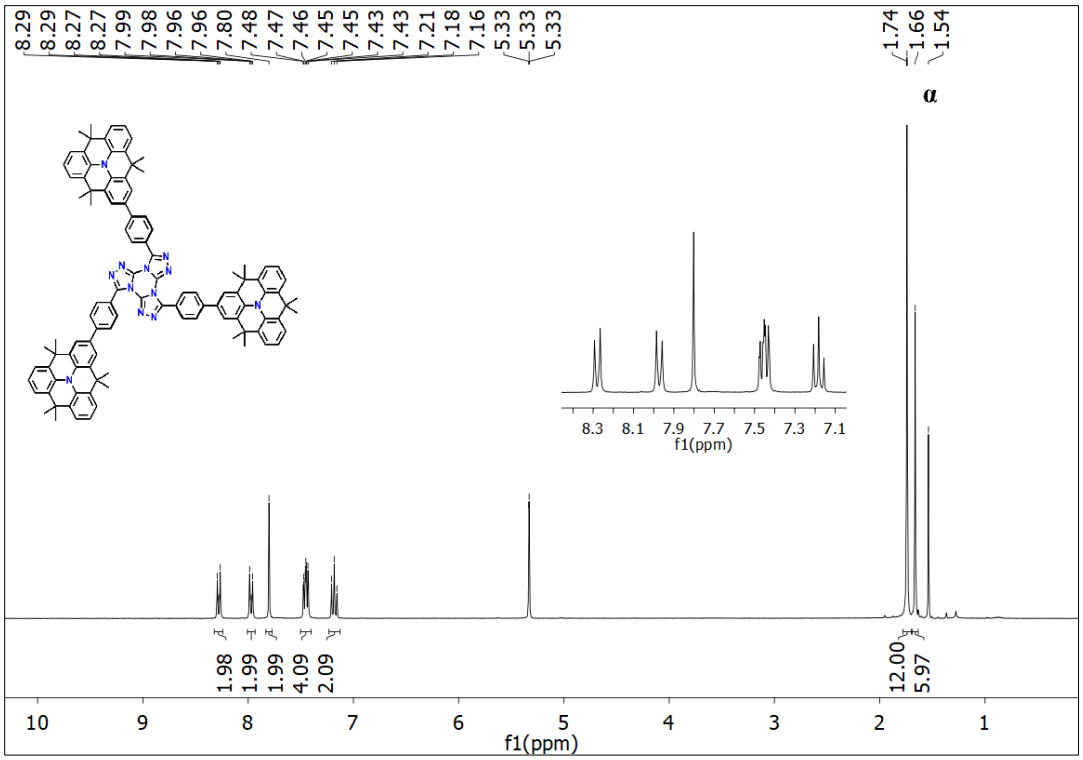


Figure S9. ^{1}H NMR (300 MHz) of **TTT-3PhHMAT** (**7**) in CD_2Cl_2.

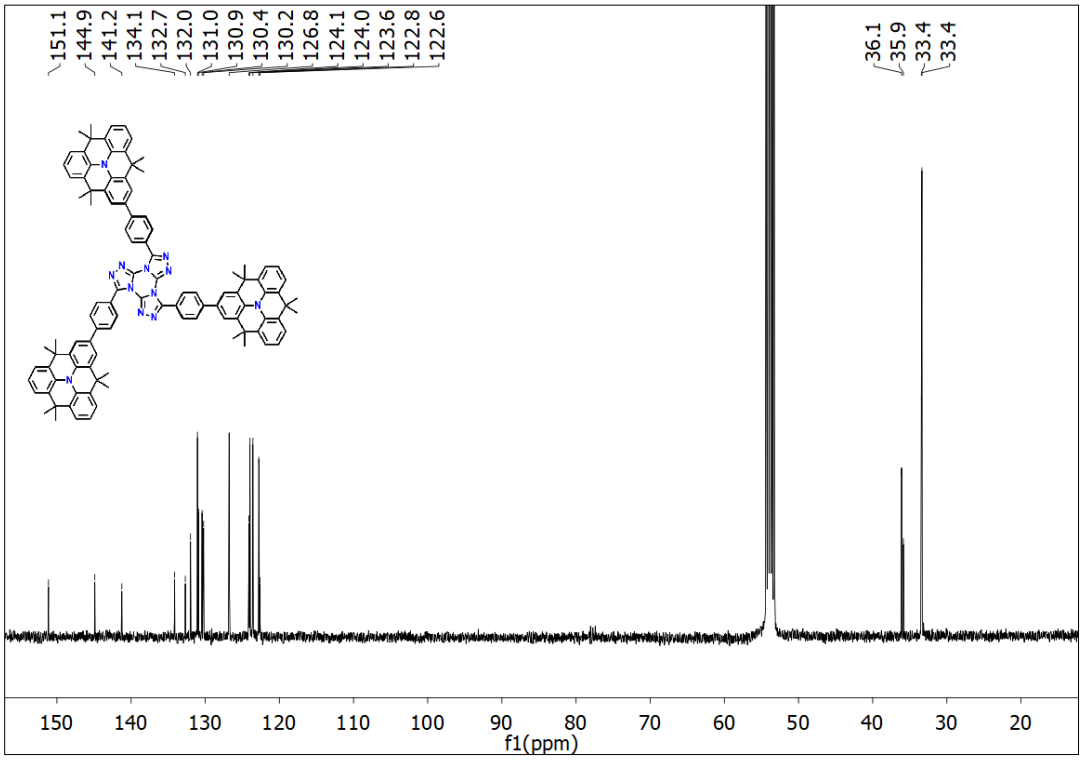


Figure S10. ^{13}C{^{1}H} NMR (101 MHz) of **TTT-3PhHMAT** (**7**) in CD_2Cl_2.

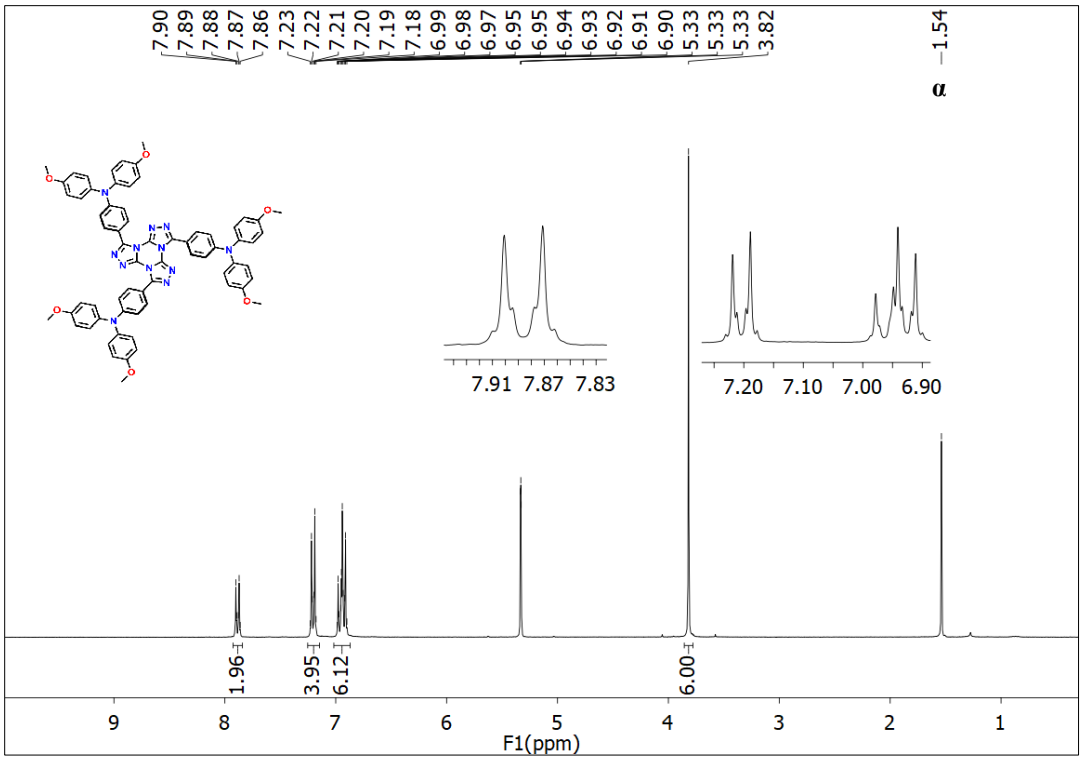


Figure S11. ^{1}H NMR (300 MHz) of **TTT-3MeO** (**8**) in CD_2Cl_2.

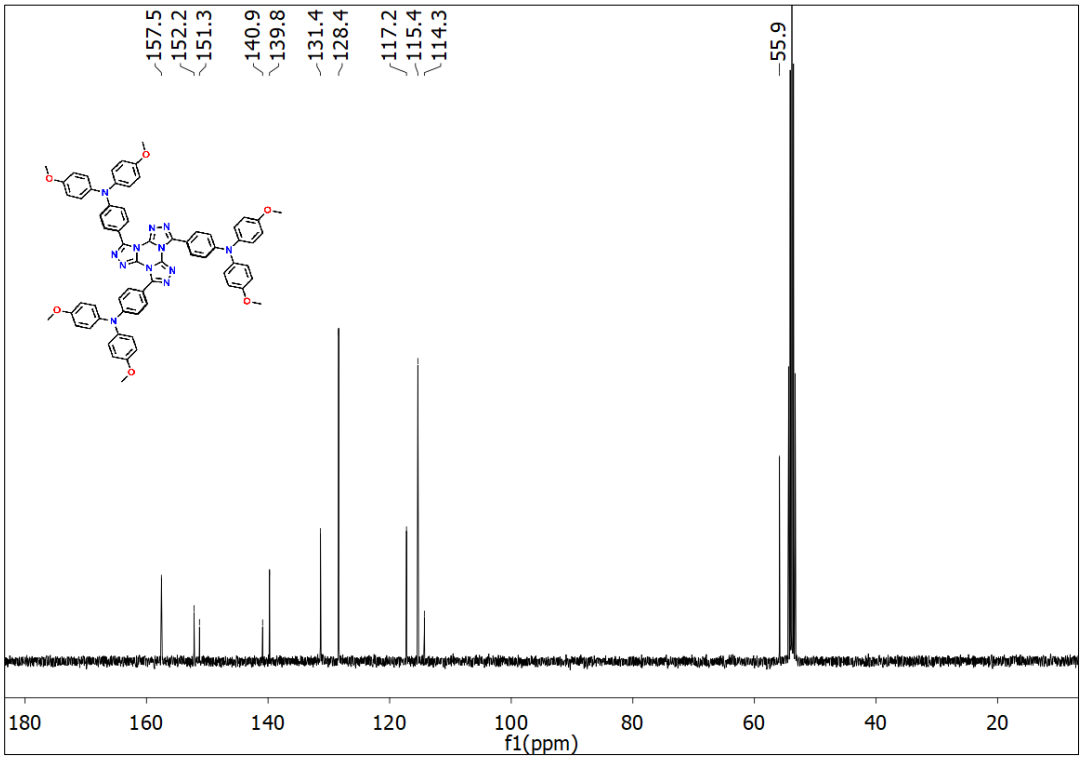


Figure S12. ^{13}C{^{1}H} NMR (101 MHz) of **TTT-3MeO** (**8**) in CD_2Cl_2.

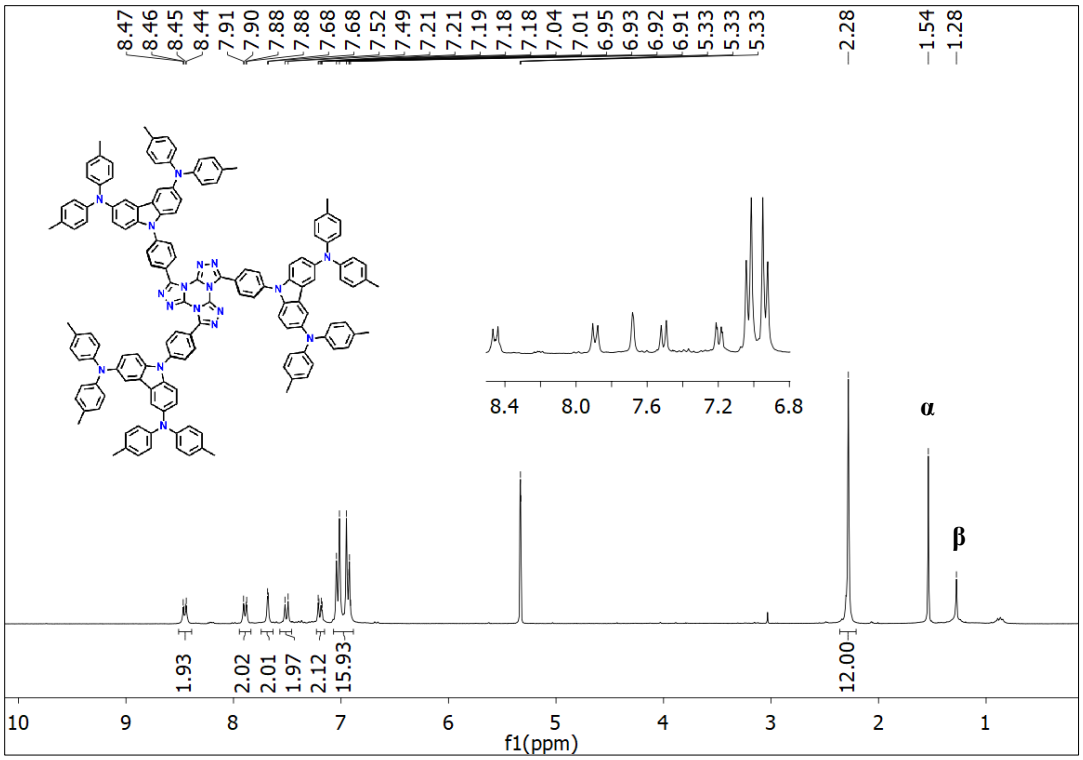


Figure S13. ^{1}H NMR (300 MHz) of **TTT-3TTAC** (**9**) in CD_2Cl_2.

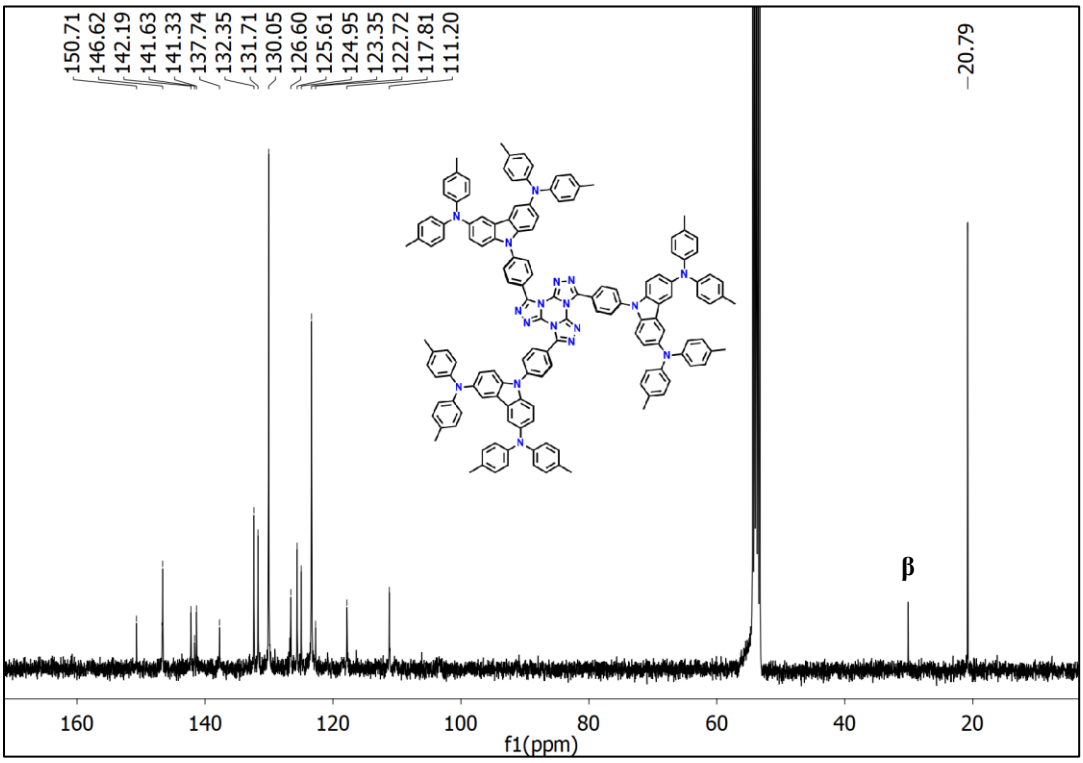
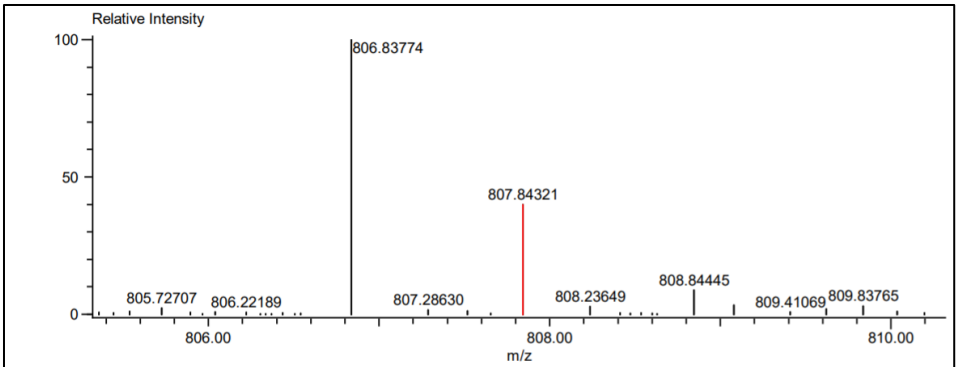
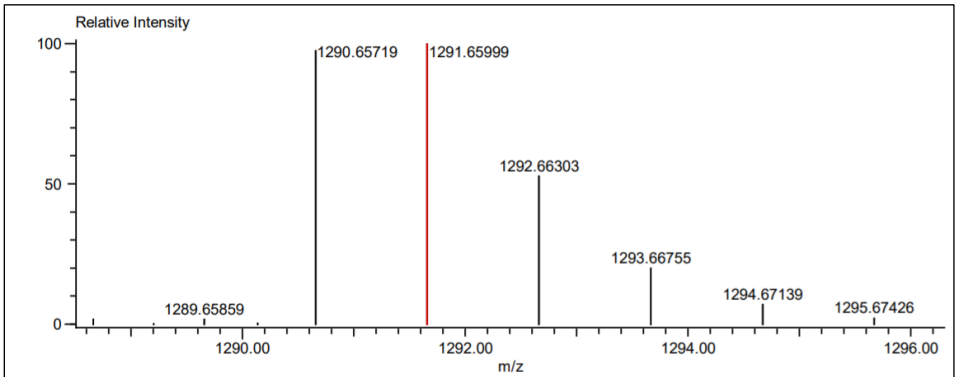


Figure S14. ^{13}C{^{1}H} NMR (101 MHz) of **TTT-3TTAC** (**9**) in CD_2Cl_2.



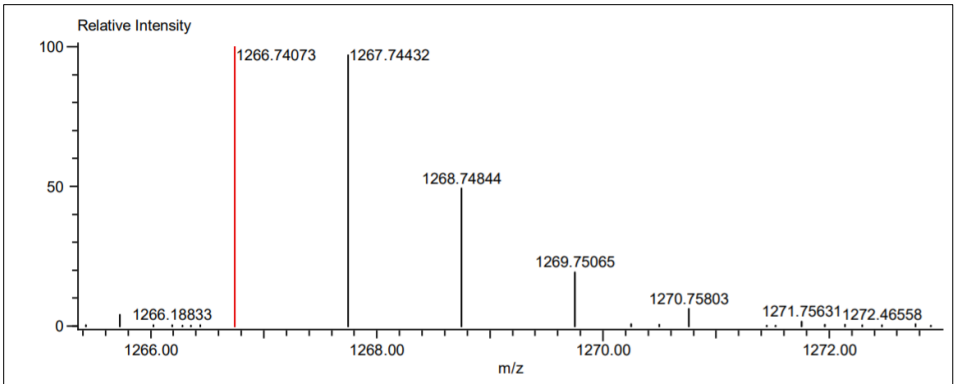
Mass	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
807.84321	807.84303	0.18	0.23	$^{12}C_{39}{}^{1}H_{2}{}^{127}I_{2}{}^{14}N_{6}$	41.0
	807.84279	0.42	0.52	$^{12}C_{24}{}^{1}H_{13}{}^{127}I_{3}{}^{14}N_{9}$	21.5

Figure S15. FD^{+} high resolution mass spectrum of **TTT-3PhI (4)**



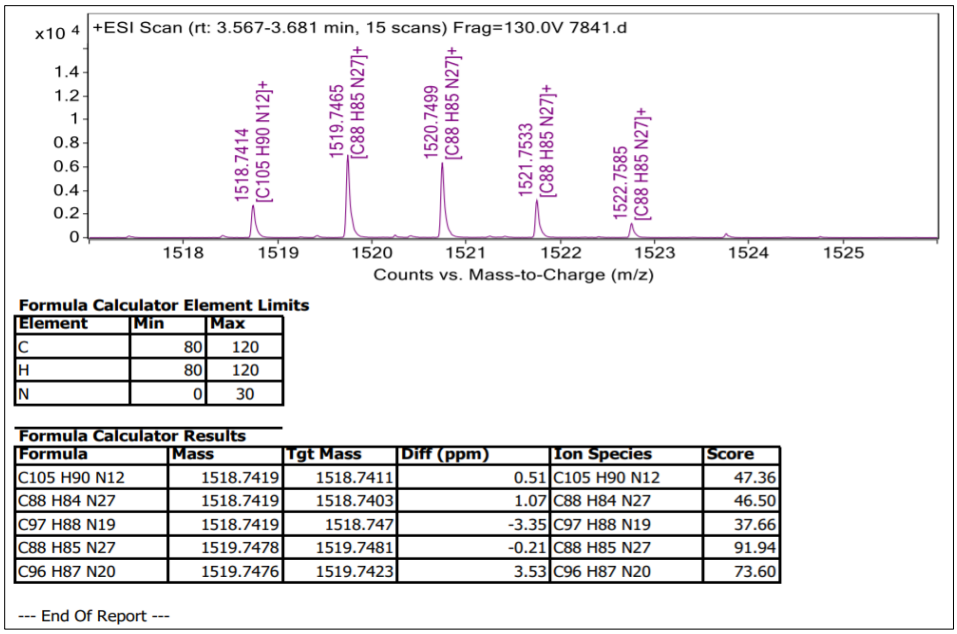
Mass	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
1291.65999	1291.66177	-1.78	-1.38	$^{12}C_{96}{}^{1}H_{83}{}^{14}N_{4}$	57.5
	1291.65506	4.93	3.81	$^{12}C_{87}{}^{1}H_{79}{}^{14}N_{12}$	54.5

Figure S16. FD^{+} high resolution mass spectrum of **TTT-3HMAT (5)**



Mass	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
1266.74073	1266.74114	-0.41	-0.32	$^{12}C_{84}{}^{1}H_{90}{}^{14}N_{12}$	46.0
	1266.73527	5.46	4.31	$^{12}C_{92}{}^{1}H_{92}{}^{14}N_{5}$	49.5

Figure S17. FD^{+} high resolution mass spectrum of **TTT-3tBu (6)**



Formula Calculator Element Limits

Element	Min	Max
C	80	120
H	80	120
N	0	30

Formula Calculator Results

Formula	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C105 H90 N12	1518.7419	1518.7411	0.51	C105 H90 N12	47.36
C88 H84 N27	1518.7419	1518.7403	1.07	C88 H84 N27	46.50
C97 H88 N19	1518.7419	1518.747	-3.35	C97 H88 N19	37.66
C88 H85 N27	1519.7478	1519.7481	-0.21	C88 H85 N27	91.94
C96 H87 N20	1519.7476	1519.7423	3.53	C96 H87 N20	73.60

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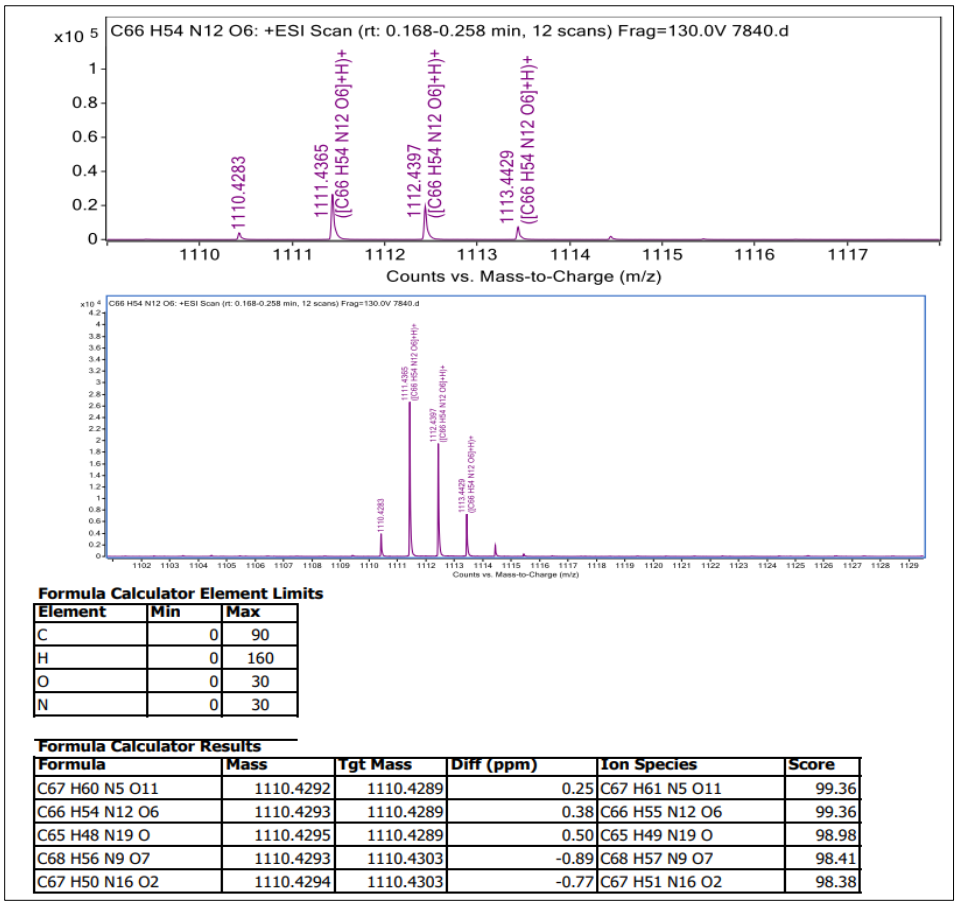
Figure S18. ESI^+ high resolution mass spectrum of **TTT-3PhHMAT (7)**



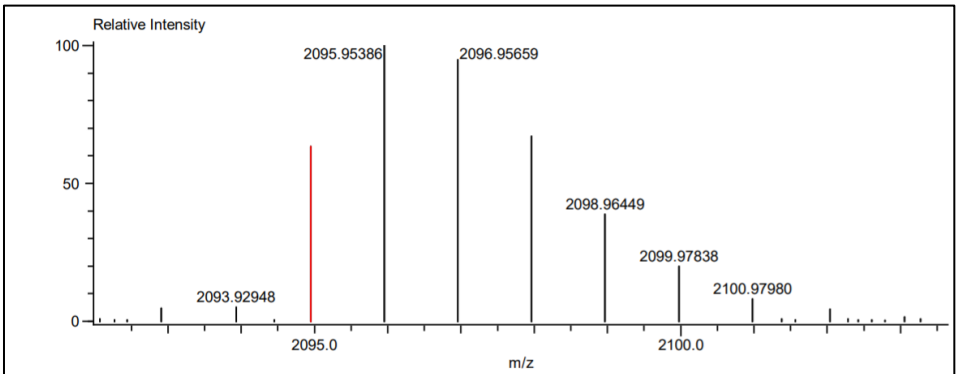
Formula Calculator Element Limits

Element	Min	Max
C	0	90
H	0	160
O	0	30
N	0	30

Formula Calculator Results

Formula	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C67 H60 N5 O11	1110.4292	1110.4289	0.25	C67 H61 N5 O11	99.36
C66 H54 N12 O6	1110.4293	1110.4289	0.38	C66 H55 N12 O6	99.36
C65 H48 N19 O	1110.4295	1110.4289	0.50	C65 H49 N19 O	98.98
C68 H56 N9 O7	1110.4293	1110.4303	-0.89	C68 H57 N9 O7	98.41
C67 H50 N16 O2	1110.4294	1110.4303	-0.77	C67 H51 N16 O2	98.38

Figure S19. ESI^+ high resolution mass spectrum of **TTT-3MeO (8)**



Mass	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
2094.94675	2094.94738	-0.63	-0.30	$^{12}C_{144}{}^{1}H_{114}{}^{14}N_{18}$	97.0
	2094.95409	-7.34	-3.50	$^{12}C_{153}{}^{1}H_{118}{}^{14}N_{10}$	100.0

Figure S20. FD^{+} high resolution mass spectrum of **TTT-3TTAC (9)**

Photophysical Electrochemical and Thermal Characterization

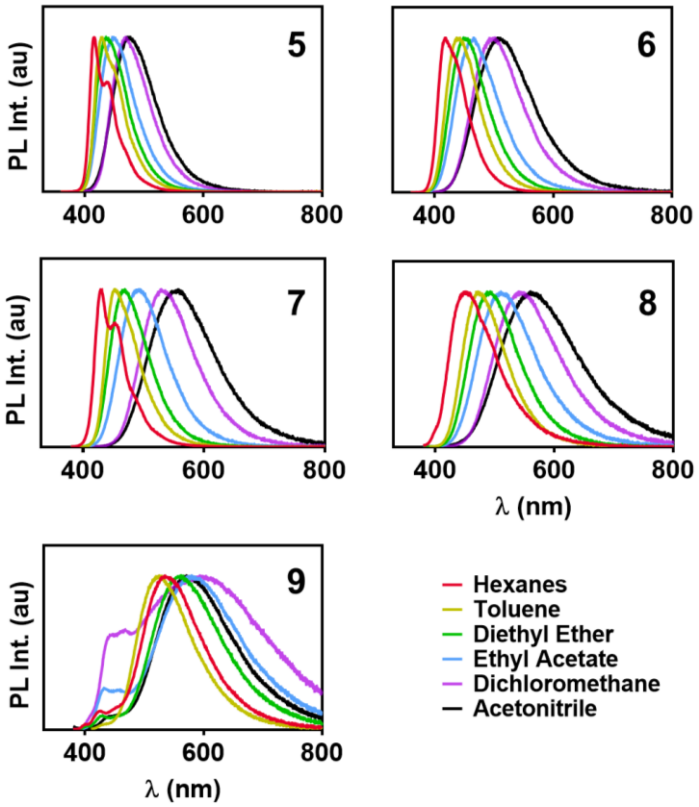


Figure S21. Normalized emission spectra showing solvatochromic shifts for compound **5-9**, measured at concentrations of 1 x 10^{-2} mg mL^{-1} in toluene, and excited at 350 nm.

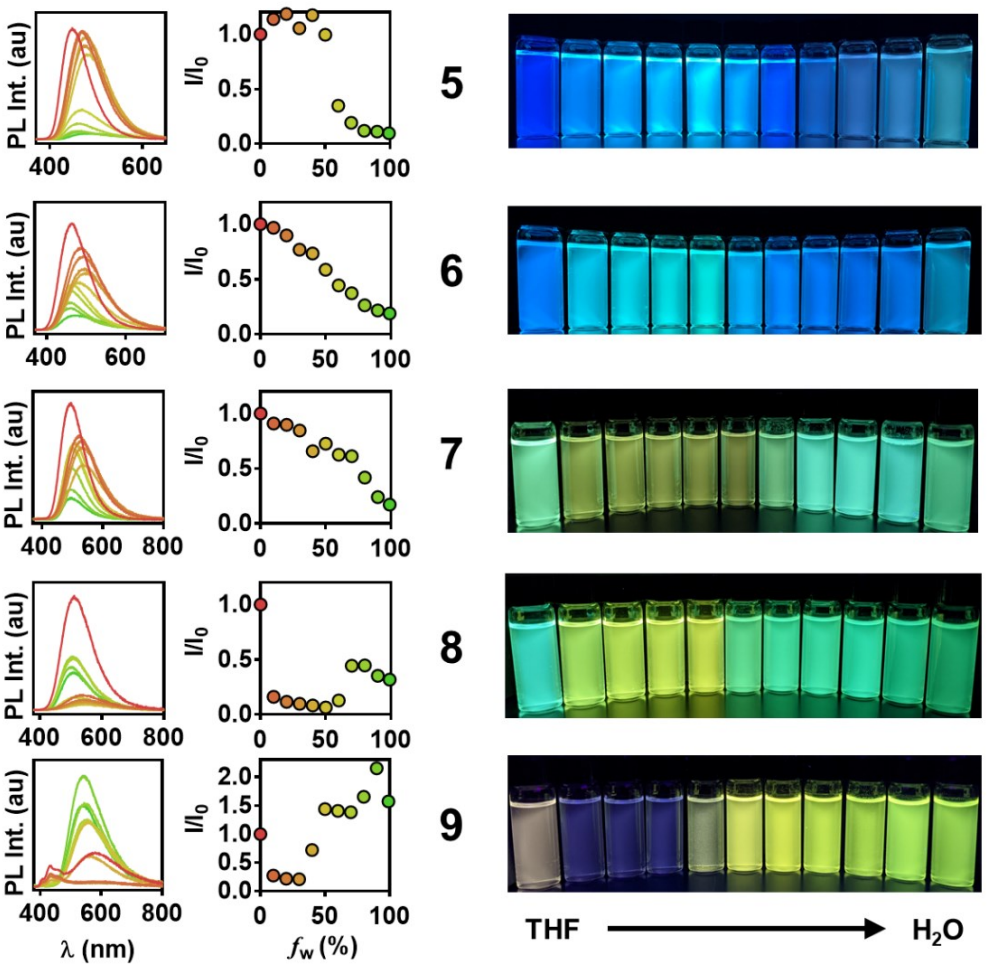


Figure S22. Emission spectra (left column), and relative emission intensity (I/I_0) as a function of water fraction f_w (middle column) for solutions of emitters **5**-**9** in THF/water solutions ranging from 0% (red) to 99% (green) water. Samples were prepared as 1 x 10^{-2} mg mL^{-1} solutions and were excited at 350 nm. Images of the vial solutions are pictured under 365 nm excitation (right column).

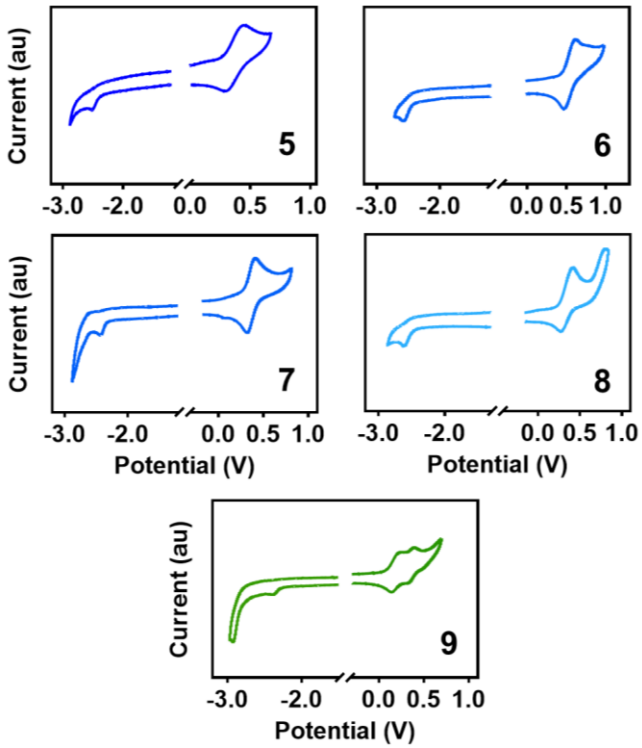


Figure S23. Cyclic voltammograms measured at 2 mg/mL in degassed *N,N*-dimethylformamide relative to $Fc^{0/+}$, with 0.02 M tetrabutylammonium hexafluorophosphate. The third oxidative and reductive cycles in each case are shown.

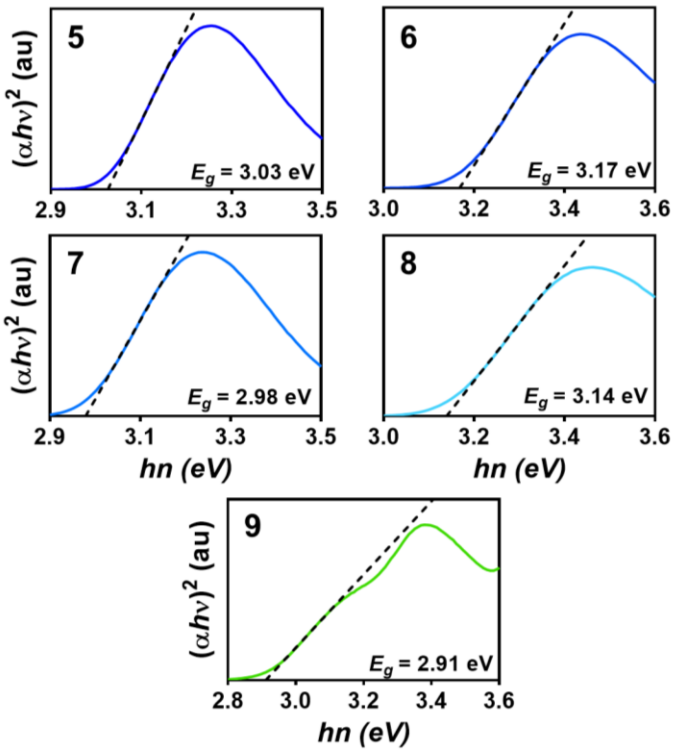


Figure S24. Tauc plots of compounds **5-9** with calculated optical gaps (E_g) displayed inset.

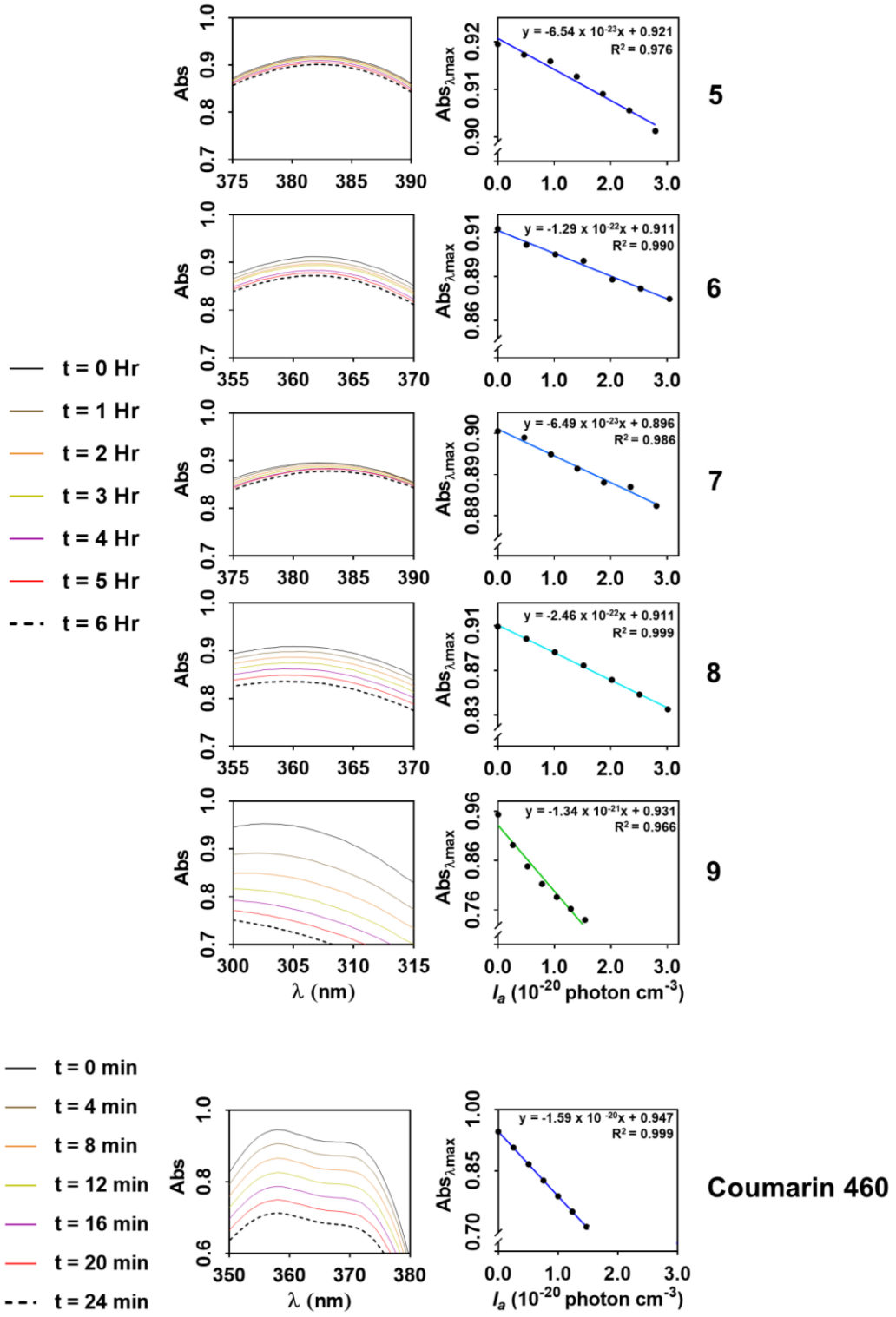


Figure S25. (Left column) UV-Vis of emitters **5-9** and **Coumarin 460** dye standard, and the corresponding decrease of absorbance from irradiation time intervals of 1 hour (zoomed in to λ_{max} for visualization). (Right column) Photodestructive quantum yield experiments for **5-9** and **Coumarin 460** dye standard, with absorbance at λ_{max} plotted as a function of total absorbed light intensity (λ_{exc} = 365 nm) over six hours of sample exposure.

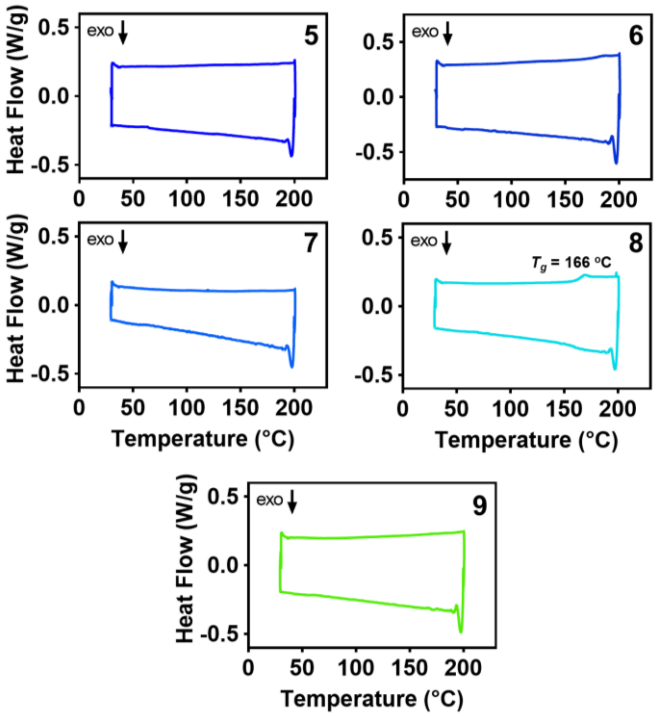


Figure S26. Differential scanning calorimetry (DSC) traces acquired at a rate of 10 °C min^{-1}, under a 50 mL min^{-1} flow of nitrogen gas. Two consecutive heating and cooling cycles were performed, with the third cycle shown in each case.

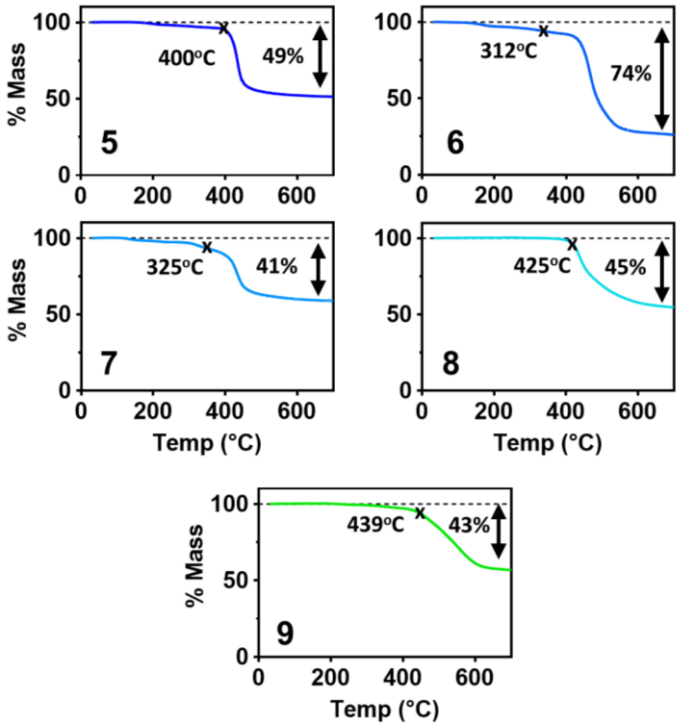


Figure S27. Thermogravimetric analysis (TGA) performed at a rate of 10 °C min^{-1}, under a 50 mL min^{-1} flow of nitrogen gas, from 30 to 700 °C.

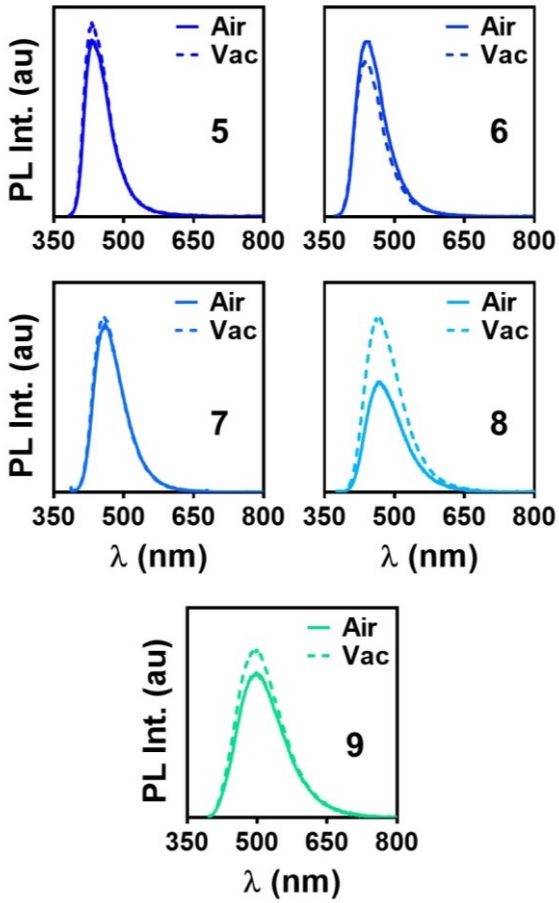


Figure S28. Emission spectra measured in 4 wt.% doped PMMA films under air (solid trace) compared to vacuum (dashed trace), for emitters **5-9** with 350 nm excitation.

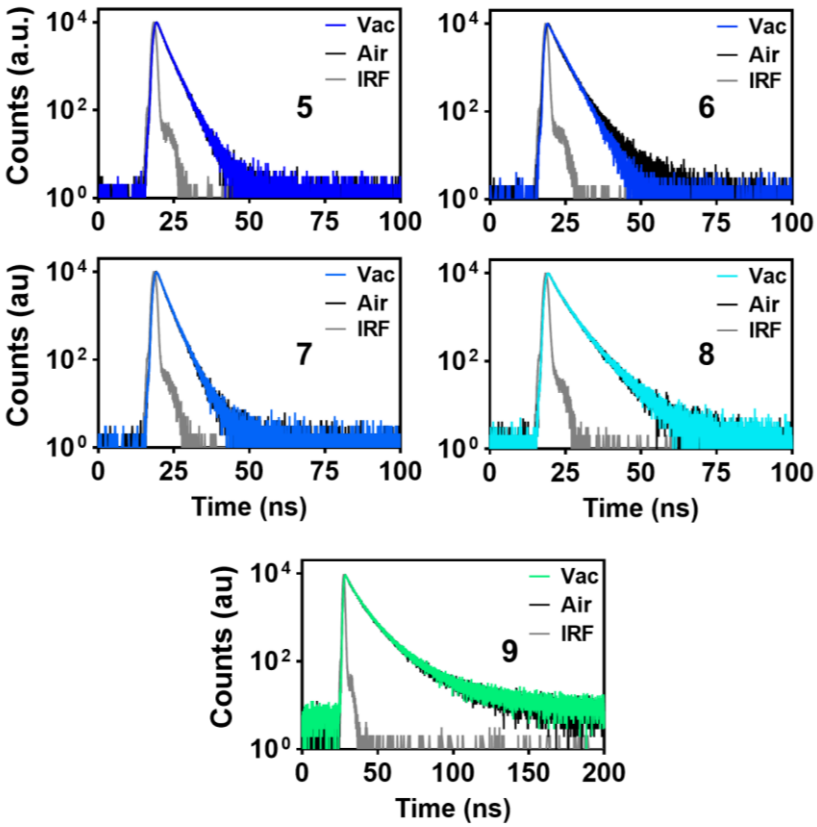


Figure S29. PL decays for 4 wt.% doped PMMA films of emitters **5-9** under air (black trace) or vacuum (colored trace). All measurements were performed using TCSPC with a 313 nm EPLED source.

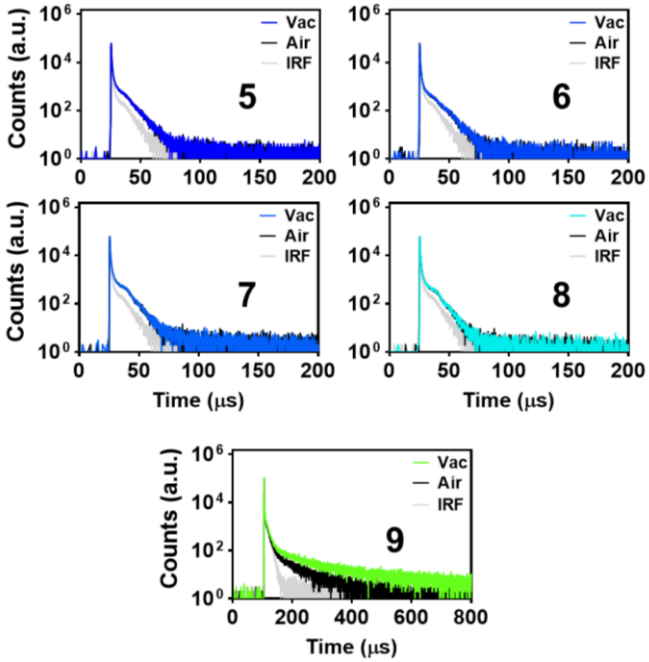


Figure S30. PL decays for 4 wt% doped PMMA films of emitters **5-9** under air and vacuum. All measurements were performed using MCS with a 313 nm Xe μF source.

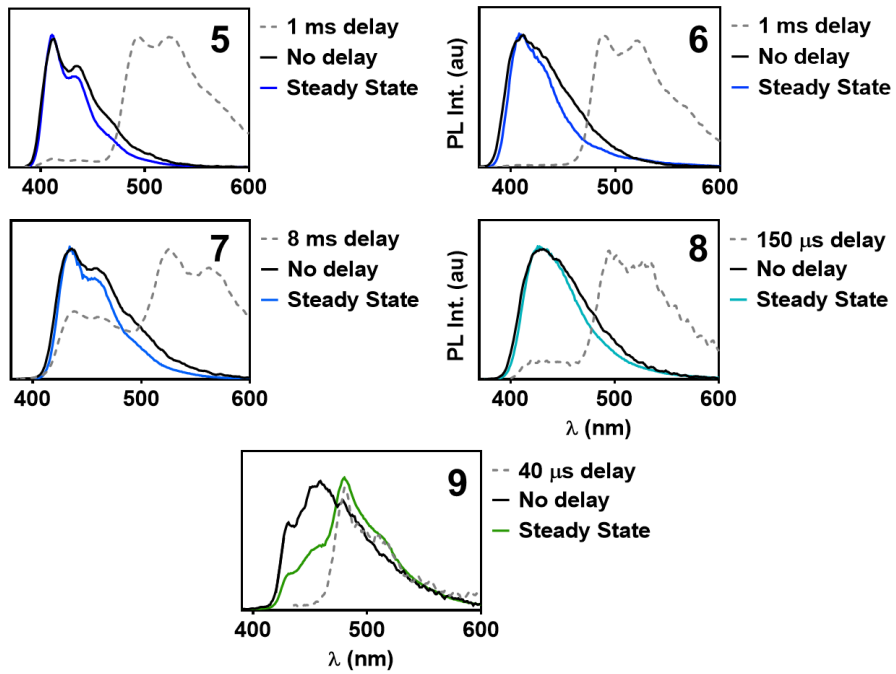


Figure S31. Time-resolved and steady-state emission (no delay = black trace; delayed = grey dashed trace, steady state colored) spectra measured in 2-methyltetrahydrofuran at 77 K for compounds **5-9**.

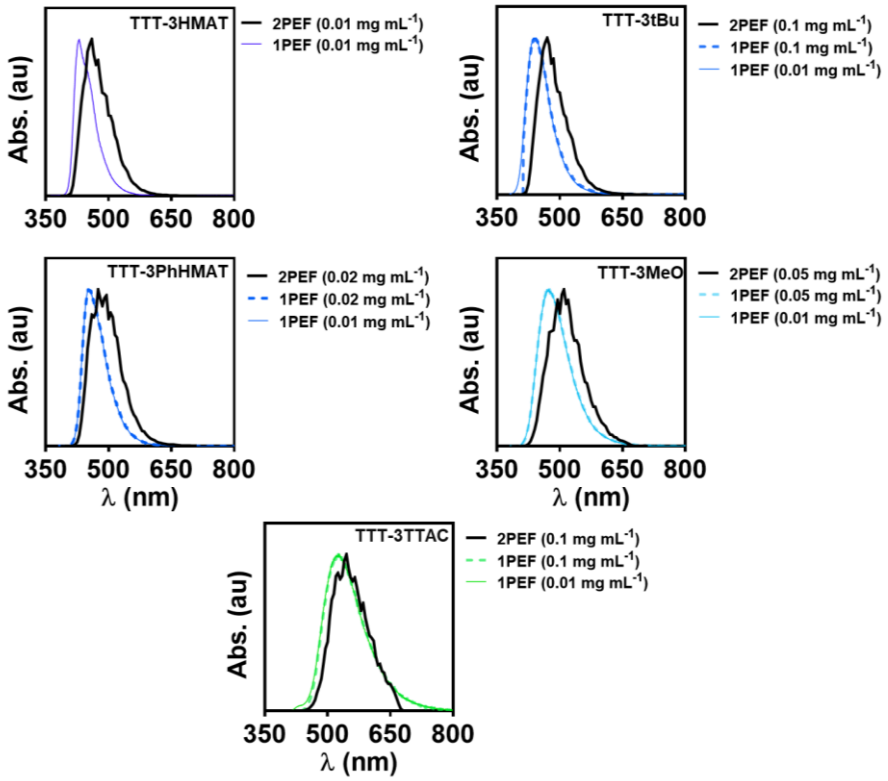


Figure S32. Comparison of one-photon excited fluorescence (1PEF) to 2PEF of respective emitters, dependent on concentration.

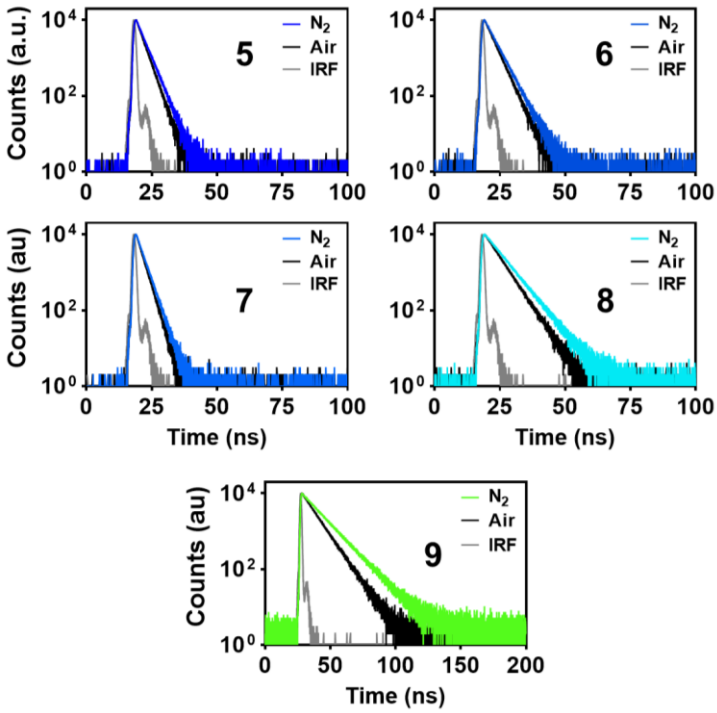


Figure S33. PL decays for toluene solutions at 1 x 10^{-2} mg mL^{-1} of emitters **5-9**, under air (black trace) or N_2 (colored trace). All measurements were performed using TCSPC with a 313 nm EPLED source.

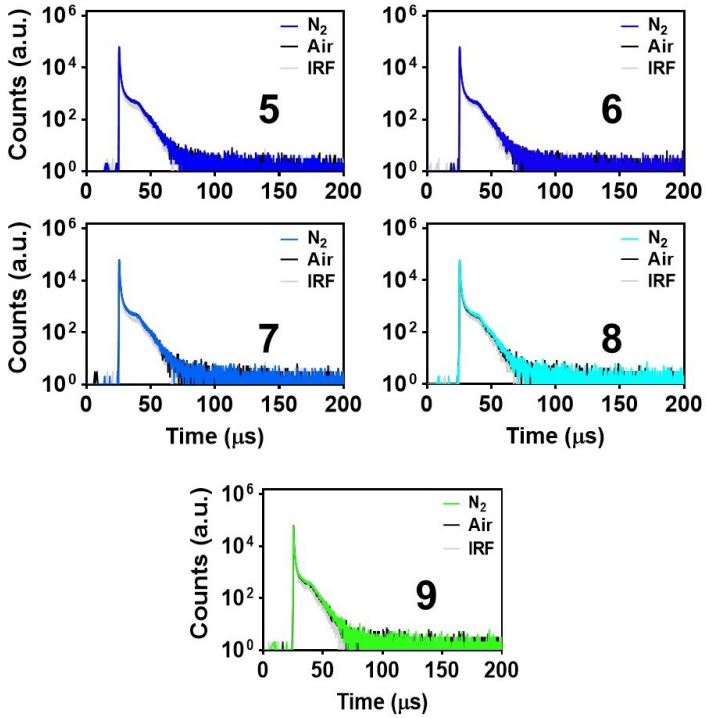


Figure S34. PL decays for toluene solutions at 1 x 10^{-2} mg mL^{-1} of emitters **5-9** under air (black trace) or N_2 (coloured trace). All measurements were performed using MCS with a 313 nm Xe μF source.

Table S1. Results of DFT and TDA-DFT calculations for **5-9**.

Entry	HOMO[a] (eV)	LUMO[a] (eV)	E_{gap} (eV)	E_{S1}[b] (eV)	f[b] ($S_0 \rightarrow S_1$)	# Imag. Freq.	E_{Total} (10^3 Hartrees)
5	-4.90	-1.60	3.30	2.87	0.752	0	-4.02
6	-4.98	-1.49	3.49	3.06	0.982	0	-3.91
7	-4.81	-1.75	3.06	2.74	0.726	0	-4.71
8	-4.81	-1.41	3.40	2.98	0.917	0	-3.66
9	-4.72	-1.91	2.81	2.56	0.249	0	-7.93

[a] Calculated at the B3LYP/6-31g+(d) level. [b] Calculated using TDA-DFT at the B3LYP/6-31g(d) level in toluene using PCM.

Table S2. Cartesian coordinates [Å] of the optimized structure for **TTT-3HMAT** (**5**).

	X	Y	Z		X	Y	Z		X	Y	Z
N	0.1970	1.3649	0.0469	**C**	6.2078	-2.3654	-0.0067	**H**	-7.8681	-1.9040	0.3777
C	1.3012	0.5210	-0.0019	**C**	5.5953	-1.2517	0.6150	**H**	-7.1121	-0.7319	-0.7163
N	1.0842	-0.8533	0.0465	**C**	6.3700	-0.1433	1.3053	**H**	-8.6374	-1.5026	-1.1682
C	-0.1988	-1.3876	-0.0028	**C**	3.9933	-3.1318	-0.6501	**H**	-7.5741	-2.3404	-3.3821
N	-1.2804	-0.5126	0.0464	**C**	3.3805	-2.0348	-0.0394	**H**	-6.0516	-1.5604	-2.9388
C	-1.1016	0.8657	-0.0018	**C**	4.2096	-1.1135	0.5946	**H**	-6.0783	-3.2906	-3.3281
C	-2.6759	-0.6744	-0.0390	**C**	11.3598	-3.6393	1.1681	**H**	9.8436	-6.7744	-2.3529
N	-3.2242	0.5231	-0.1161	**C**	11.5643	-2.3363	-1.0011	**H**	7.3910	-6.4628	-2.3803
N	-2.2385	1.4895	-0.0996	**C**	5.8928	-0.0293	2.7782	**H**	11.2442	-5.0891	-1.2097
C	1.9221	-1.9808	-0.0399	**C**	6.0955	1.1922	0.5611	**H**	8.2362	1.3780	2.3762
N	1.1593	-3.0543	-0.1184	**C**	5.2843	-5.8114	-0.6808	**H**	10.6930	1.1037	2.4424
N	-0.1705	-2.6840	-0.1019	**C**	5.4678	-4.4984	-2.8458	**H**	11.6985	-0.8789	1.3622
C	0.7546	2.6543	-0.0386	**C**	0.4272	11.0877	-1.8716	**H**	3.3588	-3.8610	-1.1371
N	2.0657	2.5304	-0.1164	**C**	0.9558	9.8058	-1.8813	**H**	3.7739	-0.2497	1.0710
N	2.4098	1.1937	-0.1002	**C**	0.3059	8.7294	-1.2708	**H**	10.6711	-4.0281	1.9253
C	-9.8184	-5.1721	-1.8675	**C**	-0.9321	8.9371	-0.6196	**H**	11.9166	-4.4824	0.7482
C	-8.9722	-4.0735	-1.8776	**C**	-1.4757	10.2419	-0.6051	**H**	12.0776	-2.9806	1.6659
C	-7.7146	-4.0988	-1.2683	**C**	-0.7856	11.2854	-1.2296	**H**	12.1252	-3.1492	-1.4715
C	-7.2751	-5.2752	-0.6180	**N**	-1.6170	7.8548	0.0082	**H**	11.0209	-1.7982	-1.7847
C	-8.1336	-6.3981	-0.6031	**C**	-2.8661	8.0835	0.6599	**H**	12.2878	-1.6483	-0.5539
C	-9.3830	-6.3216	-1.2265	**C**	-3.4367	9.3759	0.6945	**H**	6.0696	-0.9696	3.3111
N	-5.9948	-5.3278	0.0085	**C**	-2.7926	10.5968	0.0621	**H**	6.4252	0.7674	3.3054
C	-5.5679	-6.5243	0.6592	**C**	-3.5610	7.0213	1.2831	**H**	4.8246	0.2003	2.8302
C	-6.4022	-7.6645	0.6941	**C**	-4.7862	7.2695	1.9082	**H**	6.6071	2.0257	1.0526

C	-7.7823	-7.7164	0.0633	**C**	-5.3508	8.5355	1.9471	**H**	6.4593	1.1304	-0.4700
C	-4.2999	-6.5957	1.2809	**C**	-4.6627	9.5733	1.3377	**H**	5.0266	1.4188	0.5284
C	-3.9018	-7.7813	1.9049	**C**	0.9967	7.3797	-1.3520	**H**	5.5843	-5.8624	0.3710
C	-4.7163	-8.9030	1.9442	**C**	0.1858	6.3081	-0.6450	**H**	4.1914	-5.7921	-0.7231
C	-5.9597	-8.8253	1.3363	**C**	-1.0549	6.5583	-0.0065	**H**	5.6218	-6.7265	-1.1765
C	-6.8909	-2.8258	-1.3497	**C**	-1.7136	5.4711	0.6149	**H**	4.3789	-4.4554	-2.9432
C	-5.5568	-2.9930	-0.6441	**C**	-3.0610	5.5880	1.3048	**H**	5.8904	-3.6121	-3.3305
C	-5.1528	-4.1930	-0.0065	**C**	0.7164	5.0235	-0.6487	**H**	5.8160	-5.3826	-3.3879
C	-3.8812	-4.2204	0.6136	**C**	0.0722	3.9444	-0.0384	**H**	0.9475	11.9113	-2.3513
C	-3.3083	-5.4463	1.3020	**C**	-1.1405	4.2019	0.5949	**H**	1.9042	9.6316	-2.3774
C	-4.7093	-1.8913	-0.6480	**C**	-2.5298	11.6578	1.1653	**H**	-1.2136	12.2816	-1.2105
C	-3.4522	-1.9102	-0.0389	**C**	-3.7579	11.1812	-1.0050	**H**	-5.3124	6.4437	2.3740
C	-3.0684	-3.0897	0.5934	**C**	-2.9217	5.1183	2.7778	**H**	-6.3037	8.7083	2.4385
C	-8.8315	-8.0192	1.1675	**C**	-4.0800	4.6822	0.5605	**H**	-5.0891	10.5701	1.3582
C	-7.8074	-8.8442	-1.0041	**C**	2.3918	7.4813	-0.6778	**H**	1.6654	4.8385	-1.1351
C	-2.9693	-5.0918	2.7749	**C**	1.1646	6.9840	-2.8439	**H**	-1.6710	3.3927	1.0711
C	-2.0153	-5.8759	0.5560	**H**	-10.7923	-5.1328	-2.3463	**H**	-1.8495	11.2566	1.9235
C	-7.6755	-1.6686	-0.6741	**H**	-9.2958	-3.1648	-2.3730	**H**	-2.0781	12.5614	0.7452
C	-6.6335	-2.4818	-2.8416	**H**	-10.0319	-7.1901	-1.2070	**H**	-3.4599	11.9501	1.6618
C	9.3903	-5.9123	-1.8728	**H**	-2.9231	-7.8246	2.3695	**H**	-3.3340	12.0732	-1.4757
C	8.0158	-5.7290	-1.8833	**H**	-4.3892	-9.8150	2.4348	**H**	-3.9511	10.4408	-1.7881
C	7.4083	-4.6285	-1.2721	**H**	-6.6101	-9.6928	1.3572	**H**	-4.7160	11.4639	-0.5590
C	8.2068	-3.6607	-0.6197	**H**	-5.0239	-0.9766	-1.1336	**H**	-2.1959	5.7417	3.3107
C	9.6086	-3.8425	-0.6044	**H**	-2.1019	-3.1450	1.0686	**H**	-3.8779	5.1811	3.3047
C	10.1675	-4.9615	-1.2295	**H**	-8.8230	-7.2296	1.9260	**H**	-2.5863	4.0784	2.8303
N	7.6117	-2.5269	0.0085	**H**	-9.8403	-8.0791	0.7485	**H**	-3.7417	3.6431	0.5283
C	8.4339	-1.5598	0.6612	**H**	-8.6194	-8.9710	1.6635	**H**	-5.0578	4.7085	1.0517
C	9.8385	-1.7121	0.6966	**H**	-8.7924	-8.9226	-1.4738	**H**	-4.2081	5.0277	-0.4708
C	10.5740	-2.8802	0.0644	**H**	-7.0705	-8.6414	-1.7880	**H**	2.2851	7.7664	0.3740
C	7.8612	-0.4271	1.2844	**H**	-7.5731	-9.8155	-0.5587	**H**	2.9215	6.5251	-0.7198
C	8.6885	0.5095	1.9104	**H**	-3.8713	-4.7749	3.3090	**H**	3.0159	8.2311	-1.1728
C	10.0671	0.3652	1.9502	**H**	-2.5452	-5.9518	3.3008	**H**	1.7567	7.7277	-3.3853
C	10.6220	-0.7495	1.3408	**H**	-2.2360	-4.2817	2.8270	**H**	1.6718	6.0194	-2.9410

C	5.8940	-4.5520	-1.3539	**H**	-1.2844	-5.0636	0.5234	**H**	0.1862	6.9070	-3.3294
C	5.3711	-3.3145	-0.6462	**H**	-1.5489	-6.7363	1.0460	**H**	-2.2518	-6.1588	-0.4753

Table S3. Cartesian coordinates [Å] of the optimized structure for **TTT-3tBu** (**6**).

	X	Y	Z		X	Y	Z		X	Y	Z
C	7.5706	-6.6363	-0.7548	**C**	-11.1976	0.2016	5.6990	**H**	2.1952	-2.9195	-1.4320
C	6.8892	-7.6058	-1.5026	**C**	-6.5592	0.9299	0.0798	**H**	3.6865	-4.8520	-1.5767
C	5.5097	-7.7885	-1.3853	**C**	-5.9790	1.9248	-0.7304	**H**	-10.9823	-1.8332	2.3725
C	4.7653	-7.0100	-0.4946	**C**	-4.6009	2.0666	-0.7927	**H**	-9.8709	-1.0717	0.3269
C	5.4312	-6.0440	0.2732	**C**	-3.7513	1.2240	-0.0509	**H**	-7.4583	1.6296	2.6288
C	6.8027	-5.8610	0.1323	**C**	-4.3318	0.2412	0.7665	**H**	-8.5485	0.8578	4.6836
N	3.3637	-7.2084	-0.3584	**C**	-5.7112	0.0936	0.8278	**H**	-7.4784	0.0089	-2.3820
C	2.8645	-8.5377	-0.2881	**C**	8.7169	7.0625	1.0269	**H**	-8.8723	0.4698	-4.3410
C	1.7485	-8.9271	-1.0346	**C**	7.7197	7.8462	1.6231	**H**	-11.6672	2.5821	-1.8442
C	1.2671	-10.2355	-0.9574	**C**	6.3647	7.6376	1.3580	**H**	-10.2521	2.1353	0.1084
C	1.8873	-11.2033	-0.1555	**C**	5.9627	6.6386	0.4670	**H**	-11.4274	1.5421	-6.6043
C	3.0152	-10.7944	0.5779	**C**	6.9462	5.8525	-0.1499	**H**	-9.7651	1.7209	-6.0272
C	3.4955	-9.4899	0.5242	**C**	8.2915	6.0603	0.1369	**H**	-10.6517	0.2073	-5.7413
C	1.3904	-12.6513	-0.0545	**N**	4.5851	6.4380	0.1788	**H**	-13.3598	1.4649	-5.0719
C	0.1521	-12.9069	-0.9306	**C**	3.7648	7.5734	-0.0682	**H**	-13.1688	1.6608	-3.3218
C	2.5109	-13.6120	-0.5122	**C**	4.2130	8.6067	-0.8956	**H**	-12.6261	0.1677	-4.1040
C	1.0162	-12.9639	1.4119	**C**	3.4142	9.7296	-1.1211	**H**	-10.4628	3.8654	-4.8048
C	9.0822	-6.3997	-0.8677	**C**	2.1416	9.8560	-0.5482	**H**	-12.0901	3.6375	-5.4815
C	9.7465	-7.3405	-1.8874	**C**	1.7078	8.8036	0.2775	**H**	-11.8763	3.8674	-3.7382
C	9.3412	-4.9434	-1.3151	**C**	2.4999	7.6876	0.5257	**H**	-12.0408	-2.3780	5.7465
C	9.7434	-6.6369	0.5087	**C**	1.2324	11.0690	-0.7848	**H**	-12.4099	-1.7231	4.1456
C	2.4895	-6.1112	-0.2946	**C**	1.8784	12.1115	-1.7132	**H**	-11.1780	-2.9912	4.3295
C	1.3017	-6.1787	0.4593	**C**	-0.0898	10.5999	-1.4326	**H**	-9.9101	-1.9256	6.9035
C	0.4491	-5.0868	0.5288	**C**	0.9253	11.7520	0.5669	**H**	-8.6790	-0.8604	6.2057
C	0.7566	-3.8855	-0.1356	**C**	10.2134	7.2576	1.3032	**H**	-8.9578	-2.4611	5.5020
C	1.9359	-3.8229	-0.8945	**C**	10.4798	8.3968	2.3019	**H**	-11.9660	0.6357	5.0489
C	2.7845	-4.9176	-0.9787	**C**	10.8007	5.9546	1.8907	**H**	-11.6751	-0.1049	6.6379
N	1.1214	0.7185	-0.0957	**C**	10.9398	7.5954	-0.0182	**H**	-10.4730	0.9885	5.9334

C	1.2293	-0.6626	0.0053	**C**	4.0424	5.1434	0.1456	**H**	-6.6170	2.5837	-1.3094
N	0.0633	-1.4162	-0.0939	**C**	2.9670	4.8365	-0.7079	**H**	-4.1639	2.8459	-1.4081
C	-1.1916	-0.8270	-0.0036	**C**	2.4135	3.5635	-0.7261	**H**	-3.7089	-0.4321	1.3405
N	-1.2609	0.5635	-0.0174	**C**	2.9226	2.5484	0.0997	**H**	-6.1393	-0.6810	1.4544
C	-0.1196	1.3480	-0.1471	**C**	4.0131	2.8494	0.9375	**H**	7.9865	8.6326	2.3200
C	-2.3157	1.4877	-0.1085	**C**	4.5593	4.1238	0.9688	**H**	5.6140	8.2572	1.8391
N	-1.7989	2.6903	-0.2687	**H**	7.4273	-8.2322	-2.2051	**H**	6.6501	5.0778	-0.8507
N	-0.4201	2.6037	-0.3037	**H**	5.0079	-8.5431	-1.9835	**H**	9.0247	5.4310	-0.3593
C	-0.2073	-2.7928	-0.0637	**H**	4.8688	-5.4338	0.9732	**H**	5.1923	8.5333	-1.3587
N	-1.5123	-2.9570	0.0281	**H**	7.2827	-5.1001	0.7409	**H**	3.8016	10.5077	-1.7691
N	-2.1333	-1.7212	0.0732	**H**	1.2527	-8.2027	-1.6736	**H**	0.7320	8.8547	0.7517
C	2.4416	1.1703	0.0808	**H**	0.3976	-10.4932	-1.5514	**H**	2.1388	6.8958	1.1748
N	3.2189	0.1186	0.2511	**H**	3.5298	-11.5047	1.2187	**H**	1.1926	12.9551	-1.8508
N	2.4573	-1.0357	0.2141	**H**	4.3654	-9.2018	1.1066	**H**	2.8109	12.5075	-1.2945
C	-9.8615	-0.5593	3.7107	**H**	-0.1634	-13.9510	-0.8241	**H**	2.0945	11.6956	-2.7041
C	-10.2124	-1.0746	2.4558	**H**	-0.6929	-12.2740	-0.6358	**H**	-0.7530	11.4562	-1.6073
C	-9.5827	-0.6488	1.2844	**H**	0.3611	-12.7307	-1.9921	**H**	-0.6236	9.8872	-0.7954
C	-8.5832	0.3269	1.3319	**H**	2.1711	-14.6530	-0.4448	**H**	0.1007	10.1114	-2.3951
C	-8.2273	0.8648	2.5769	**H**	3.4088	-13.5122	0.1066	**H**	1.8486	12.0958	1.0475
C	-8.8512	0.4188	3.7373	**H**	2.7953	-13.4106	-1.5514	**H**	0.2731	12.6210	0.4149
N	-7.9548	0.7787	0.1395	**H**	0.2203	-12.2960	1.7609	**H**	0.4197	11.0714	1.2598
C	-8.7613	1.0457	-1.0003	**H**	0.6607	-13.9979	1.5021	**H**	11.5588	8.4957	2.4662
C	-8.3946	0.5800	-2.2664	**H**	1.8728	-12.8445	2.0835	**H**	10.1121	9.3597	1.9288
C	-9.1957	0.8486	-3.3781	**H**	10.8217	-7.1329	-1.9318	**H**	10.0131	8.2028	3.2746
C	-10.3935	1.5678	-3.2677	**H**	9.6238	-8.3938	-1.6100	**H**	11.8720	6.0770	2.0932
C	-10.7504	2.0162	-1.9837	**H**	9.3403	-7.1998	-2.8957	**H**	10.6842	5.1108	1.2026
C	-9.9535	1.7711	-0.8700	**H**	10.4191	-4.7569	-1.3990	**H**	10.3016	5.6924	2.8307
C	-11.3016	1.8722	-4.4663	**H**	8.9305	-4.2207	-0.6025	**H**	10.5417	8.5182	-0.4558
C	-10.7462	1.2986	-5.7810	**H**	8.8823	-4.7492	-2.2913	**H**	12.0128	7.7360	0.1622
C	-12.6973	1.2550	-4.2230	**H**	9.5752	-7.6652	0.8489	**H**	10.8268	6.7970	-0.7590
C	-11.4407	3.4026	-4.6290	**H**	10.8257	-6.4688	0.4453	**H**	2.5647	5.6041	-1.3597
C	-10.5250	-1.0116	5.0181	**H**	9.3441	-5.9613	1.2724	**H**	1.5832	3.3637	-1.3904
C	-11.5990	-2.0882	4.7864	**H**	1.0594	-7.0886	0.9973	**H**	4.4172	2.0708	1.5761

C	-9.4513	-1.5976	5.9625	**H**	-0.4624	-5.1466	1.1144	**H**	5.3835	4.3418	1.6391

Table S4. Cartesian coordinates [Å] of the optimized structure for **TTT-3PhHMAT** (**7**).

	X	Y	Z		X	Y	Z		X	Y	Z
N	-1.1033	0.7704	-0.0389	**C**	-8.8507	13.6470	-0.1093	**H**	9.3160	1.0753	3.6033
C	-1.2356	-0.6058	0.0951	**C**	-4.8363	9.0268	3.6400	**H**	10.7968	0.7060	4.4950
N	-0.0866	-1.3857	0.0025	**C**	-7.1398	8.0472	3.2170	**H**	10.4583	-1.8242	4.0084
C	1.1806	-0.8182	0.0405	**C**	-3.7531	9.4645	-2.9663	**H**	8.9787	-1.4526	3.1184
N	1.2760	0.5695	-0.0177	**C**	-6.0651	8.5093	-3.3984	**H**	10.2748	-2.3723	2.3325
C	0.1479	1.3732	-0.1389	**C**	-6.5300	-13.0775	3.3086	**H**	-6.4614	13.3387	-4.4339
C	2.3449	1.4680	-0.1680	**C**	-5.6832	-11.9795	3.3149	**H**	-5.5161	11.0547	-4.4070
N	1.8492	2.6751	-0.3504	**C**	-5.5293	-11.1526	2.1983	**H**	-7.2868	14.3094	-2.3156
N	0.4691	2.6173	-0.3414	**C**	-6.2548	-11.4299	1.0163	**H**	-7.0376	10.4201	4.6517
C	0.1610	-2.7651	0.0705	**C**	-7.1211	-12.5473	1.0043	**H**	-8.0029	12.6957	4.6771
N	1.4642	-2.9497	0.1337	**C**	-7.2384	-13.3443	2.1470	**H**	-8.1171	13.9631	2.5578
N	2.1083	-1.7265	0.1213	**N**	-6.1171	-10.6022	-0.1344	**H**	-4.2878	6.9325	-1.9705
C	-2.4127	1.2496	0.1412	**C**	-6.8577	-10.8938	-1.3153	**H**	-4.9675	6.6489	2.2162
N	-3.2062	0.2174	0.3449	**C**	-7.7354	-12.0014	-1.3640	**H**	-5.4904	14.3821	0.5155
N	-2.4681	-0.9508	0.3246	**C**	-7.9565	-12.9493	-0.1984	**H**	-6.6224	15.2789	-0.5126
C	3.7788	1.1763	-0.1422	**C**	-6.7317	-10.0831	-2.4675	**H**	-6.9189	15.1559	1.2251
C	-0.8173	-3.8523	0.0536	**C**	-7.4696	-10.3906	-3.6142	**H**	-8.9784	14.2924	-0.9834
C	-2.8791	2.6369	0.1317	**C**	-8.3329	-11.4744	-3.6674	**H**	-9.4289	12.7318	-0.2732
C	14.2495	-0.9295	3.6489	**C**	-8.4516	-12.2659	-2.5352	**H**	-9.2744	14.1683	0.7542
C	12.8764	-0.7413	3.6029	**C**	-4.5729	-9.9815	2.3422	**H**	-4.0569	9.6955	3.2604
C	12.2096	-0.4155	2.4183	**C**	-4.4916	-9.1793	1.0552	**H**	-5.1367	9.3808	4.6307
C	12.9445	-0.2684	1.2188	**C**	-5.2410	-9.4870	-0.1046	**H**	-4.4017	8.0297	3.7592
C	14.3452	-0.4576	1.2597	**C**	-5.0898	-8.6481	-1.2336	**H**	-7.4943	8.3774	4.1977
C	14.9645	-0.7835	2.4700	**C**	-5.8203	-8.8707	-2.5463	**H**	-7.9966	8.0183	2.5360
N	12.2893	0.0638	-0.0012	**C**	-3.6345	-8.0797	1.0565	**H**	-6.7574	7.0282	3.3286
C	13.0448	0.2101	-1.1995	**C**	-3.4739	-7.2406	-0.0451	**H**	-3.1342	10.0549	-2.2828
C	14.4474	0.0306	-1.1971	**C**	-4.2236	-7.5572	-1.1770	**H**	-3.2940	8.4775	-3.0764
C	15.2462	-0.3252	0.0445	**C**	-7.5580	-14.3859	-0.6331	**H**	-3.7366	9.9493	-3.9468
C	12.4097	0.5370	-2.4203	**C**	-9.4579	-12.9217	0.1976	**H**	-6.1036	8.9725	-4.3888

C	13.1736	0.6737	-3.5830	**C**	-4.7765	-9.0960	-3.6740	**H**	-5.6584	7.5006	-3.5173
C	14.5494	0.5004	-3.5865	**C**	-6.6737	-7.6141	-2.8682	**H**	-7.0897	8.4221	-3.0223
C	15.1663	0.1800	-2.3868	**C**	-3.1593	-10.5204	2.6917	**H**	-6.6355	-13.7082	4.1863
C	10.7045	-0.2336	2.5094	**C**	-5.0759	-9.0559	3.4833	**H**	-5.1226	-11.7535	4.2153
C	10.1106	0.1060	1.1535	**C**	4.6171	1.9637	-0.9516	**H**	-7.9062	-14.1985	2.1234
C	10.8832	0.2496	-0.0228	**C**	5.9942	1.7845	-0.9238	**H**	-7.3622	-9.7610	-4.4906
C	10.2102	0.5841	-1.2213	**C**	6.5855	0.8187	-0.0887	**H**	-8.8979	-11.6966	-4.5678
C	10.9121	0.7492	-2.5579	**C**	5.7379	0.0453	0.7228	**H**	-9.1213	-13.1186	-2.5581
C	8.7297	0.2911	1.1042	**C**	4.3581	0.2182	0.7026	**H**	-3.0909	-7.8486	1.9651
C	8.0495	0.6247	-0.0661	**C**	-2.3629	3.6253	-0.7193	**H**	-4.1055	-6.9439	-2.0627
C	8.8278	0.7649	-1.2141	**C**	-2.9077	4.9052	-0.7169	**H**	-6.5005	-14.4175	-0.9152
C	16.2916	0.7921	0.3101	**C**	-3.9825	5.2436	0.1228	**H**	-7.7163	-15.1027	0.1782
C	15.9750	-1.6757	-0.1937	**C**	-4.4994	4.2411	0.9641	**H**	-8.1501	-14.7180	-1.4911
C	10.6496	2.1831	-3.0926	**C**	-3.9613	2.9607	0.9705	**H**	-10.0937	-13.2194	-0.6416
C	10.3442	-0.2935	-3.5589	**C**	-0.4919	-5.0369	0.7374	**H**	-9.6606	-13.6050	1.0276
C	10.3943	0.9209	3.5007	**C**	-1.3501	-6.1286	0.7023	**H**	-9.7506	-11.9129	0.5065
C	10.0643	-1.5509	3.0252	**C**	-2.5597	-6.0809	-0.0147	**H**	-4.1679	-9.9800	-3.4570
C	-6.4086	12.7728	-3.5085	**C**	-2.8694	-4.8941	-0.7014	**H**	-5.2663	-9.2480	-4.6404
C	-5.8796	11.4913	-3.4833	**C**	-2.0156	-3.7970	-0.6732	**H**	-4.1068	-8.2362	-3.7709
C	-5.8000	10.7427	-2.3055	**H**	14.7491	-1.1827	4.5793	**H**	-7.2078	-7.7302	-3.8158
C	-6.2705	11.2950	-1.0914	**H**	12.3005	-0.8495	4.5154	**H**	-7.4125	-7.4440	-2.0783
C	-6.8126	12.6008	-1.1111	**H**	16.0394	-0.9261	2.4865	**H**	-6.0472	-6.7207	-2.9477
C	-6.8688	13.3087	-2.3154	**H**	12.6731	0.9224	-4.5123	**H**	-2.7932	-11.1731	1.8924
N	-6.2013	10.5530	0.1221	**H**	15.1254	0.6114	-4.5003	**H**	-2.4446	-9.7019	2.8187
C	-6.6817	11.1235	1.3353	**H**	16.2415	0.0398	-2.3700	**H**	-3.1734	-11.0953	3.6222
C	-7.2322	12.4259	1.3542	**H**	8.1622	0.2002	2.0230	**H**	-4.4047	-8.2037	3.6263
C	-7.3537	13.3040	0.1213	**H**	8.3312	0.9950	-2.1496	**H**	-6.0726	-8.6693	3.2471
C	-6.6178	10.4015	2.5498	**H**	15.7888	1.7497	0.4800	**H**	-5.1359	-9.5969	4.4324
C	-7.0949	10.9845	3.7274	**H**	16.8986	0.5642	1.1913	**H**	4.1748	2.7229	-1.5880
C	-7.6372	12.2604	3.7519	**H**	16.9699	0.9090	-0.5403	**H**	6.6244	2.4184	-1.5405
C	-7.6970	12.9633	2.5582	**H**	16.6467	-1.6160	-1.0553	**H**	6.1617	-0.7251	1.3597
C	-5.2020	9.3512	-2.4196	**H**	16.5740	-1.9606	0.6763	**H**	3.7365	-0.4087	1.3284
C	-5.1672	8.6573	-1.0691	**H**	15.2472	-2.4716	-0.3827	**H**	-1.5229	3.4081	-1.3655

C	-5.6541	9.2443	0.1224	**H**	11.0442	2.9275	-2.3934	**H**	-2.4702	5.6631	-1.3596
C	-5.5782	8.4859	1.3141	**H**	11.1298	2.3382	-4.0631	**H**	-5.3487	4.4626	1.6036
C	-6.0447	8.9997	2.6650	**H**	9.5786	2.3676	-3.2195	**H**	-4.3792	2.1926	1.6126
C	-4.6316	7.3705	-1.0407	**H**	9.2661	-0.1653	-3.6947	**H**	0.4453	-5.0918	1.2813
C	-4.5517	6.6066	0.1227	**H**	10.8183	-0.1972	-4.5402	**H**	-1.0685	-7.0415	1.2186
C	-5.0390	7.2005	1.2859	**H**	10.5233	-1.3092	-3.1914	**H**	-3.8072	-4.8169	-1.2429
C	-6.5483	14.6118	0.3513	**H**	10.8408	1.8557	3.1464	**H**	-2.2966	-2.8953	-1.2021

Table S5. Cartesian coordinates [Å] of the optimized structure for **TTT-3MeO** (**8**).

	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
C	4.2560	9.1984	0.9081	**C**	9.0093	-4.4514	0.5125	**H**	7.4981	9.5440	1.0988
C	3.1677	9.8445	1.5131	**O**	10.3571	-4.8309	3.9400	**H**	6.6721	7.9664	0.9401
C	1.8689	9.4406	1.2321	**O**	7.1169	-7.6876	-4.5900	**H**	6.6323	9.1424	-0.4125
C	1.6255	8.3952	0.3274	**C**	7.0688	-7.2212	-5.9304	**H**	-5.1309	13.0071	-0.9965
C	2.7125	7.7672	-0.2858	**C**	11.7492	-4.9652	3.6946	**H**	-5.2295	11.2289	-0.8421
C	4.0234	8.1517	0.0078	**C**	-5.6900	-3.3506	0.3170	**H**	-4.5788	12.2140	0.5072
N	0.2897	8.0025	0.0286	**C**	-4.7267	-3.9922	1.1212	**H**	-10.9690	-2.4851	-1.6842
C	-0.6615	9.0198	-0.2658	**C**	-3.4001	-3.5902	1.0882	**H**	-9.4875	-2.7013	0.3079
C	-0.3434	10.0464	-1.1689	**C**	-2.9803	-2.5351	0.2554	**H**	-6.4598	-4.4890	-2.1508
C	-1.2577	11.0549	-1.4437	**C**	-3.9389	-1.9044	-0.5548	**H**	-7.9022	-4.2547	-4.1307
C	-2.5207	11.0505	-0.8331	**C**	-5.2688	-2.3017	-0.5223	**H**	-6.8246	-2.7900	2.8462
C	-2.8493	10.0282	0.0654	**N**	-0.4675	1.3614	0.0531	**H**	-7.8275	-3.7837	4.8976
C	-1.9145	9.0295	0.3518	**C**	-1.3945	0.3310	-0.0635	**H**	-9.5339	-6.9351	2.5146
O	-3.3538	12.0790	-1.1764	**N**	-0.9340	-0.9803	0.0243	**H**	-8.5128	-5.9596	0.4977
O	5.4947	9.6591	1.2587	**C**	0.4225	-1.2646	0.1264	**H**	-10.8714	-3.3589	-6.0181
C	6.6303	9.0322	0.6799	**N**	1.3231	-0.2100	0.0065	**H**	-9.1414	-3.0395	-5.7005
C	-4.6442	12.1216	-0.5849	**C**	0.9022	1.1127	0.0681	**H**	-9.8260	-4.6683	-5.3957
C	-9.5413	-3.3494	-3.0350	**C**	2.7240	-0.1196	0.0259	**H**	-10.3391	-7.2386	6.0419
C	-9.9788	-2.9213	-1.7726	**N**	3.0549	1.1559	0.0856	**H**	-10.9343	-6.9292	4.3850
C	-9.1485	-3.0407	-0.6660	**N**	1.9106	1.9326	0.1198	**H**	-9.4601	-7.9171	4.6411
C	-7.8694	-3.6058	-0.7898	**C**	-1.5528	-2.2281	0.2239	**H**	7.1669	-8.3528	-2.1424
C	-7.4451	-4.0449	-2.0460	**N**	-0.6088	-3.1314	0.4063	**H**	6.9673	-6.8322	-0.1783
C	-8.2653	-3.9094	-3.1697	**N**	0.6334	-2.5267	0.3560	**H**	6.6537	-3.4707	-2.8261

N	-7.0341	-3.7462	0.3544	**C**	-1.2416	2.5268	-0.0768	**H**	6.8209	-4.9651	-4.7741
C	-7.5936	-4.3169	1.5324	**N**	-2.5005	2.1713	-0.2444	**H**	6.1762	-4.2988	2.3763
C	-7.4107	-3.7017	2.7819	**N**	-2.5967	0.7920	-0.2472	**H**	7.8459	-4.5832	4.2016
C	-7.9665	-4.2527	3.9285	**C**	5.7048	-3.1925	-0.1806	**H**	10.9958	-4.7289	1.2727
C	-8.7394	-5.4214	3.8496	**C**	5.9265	-1.9923	0.5236	**H**	9.3387	-4.4176	-0.5215
C	-8.9410	-6.0325	2.6068	**C**	4.9361	-1.0239	0.5960	**H**	7.1671	-8.1084	-6.5578
C	-8.3596	-5.4820	1.4606	**C**	3.6895	-1.2127	-0.0285	**H**	6.1131	-6.7249	-6.1448
O	-9.2522	-5.8784	5.0319	**C**	3.4740	-2.4042	-0.7401	**H**	7.8954	-6.5300	-6.1416
O	-10.4266	-3.1793	-4.0632	**C**	4.4604	-3.3774	-0.8133	**H**	12.2142	-5.0814	4.6748
C	-10.0297	-3.5899	-5.3634	**C**	-0.0754	6.6499	0.0114	**H**	11.9616	-5.8508	3.0812
C	-10.0397	-7.0598	5.0081	**C**	-1.1191	6.1930	-0.8189	**H**	12.1543	-4.0723	3.2005
C	7.0063	-6.7690	-3.5831	**C**	-1.4671	4.8509	-0.8392	**H**	-5.0264	-4.8077	1.7702
C	7.0533	-7.2817	-2.2781	**C**	-0.7812	3.9107	-0.0477	**H**	-2.6651	-4.1019	1.7006
C	6.9383	-6.4310	-1.1867	**C**	0.2511	4.3684	0.7869	**H**	-3.6562	-1.0800	-1.1958
C	6.7914	-5.0471	-1.3716	**C**	0.5946	5.7123	0.8208	**H**	-5.9937	-1.7907	-1.1462
C	6.7610	-4.5403	-2.6729	**H**	3.3630	10.6529	2.2108	**H**	6.8802	-1.8256	1.0123
C	6.8544	-5.3910	-3.7781	**H**	1.0297	9.9385	1.7081	**H**	5.1231	-0.0978	1.1294
N	6.6979	-4.1794	-0.2470	**H**	2.5363	6.9600	-0.9901	**H**	2.5237	-2.5899	-1.2240
C	7.6489	-4.3280	0.8017	**H**	4.8431	7.6360	-0.4786	**H**	4.2666	-4.2958	-1.3560
C	7.2329	-4.3840	2.1422	**H**	0.6311	10.0501	-1.6476	**H**	-1.6453	6.8960	-1.4552
C	8.1602	-4.5409	3.1633	**H**	-1.0178	11.8527	-2.1397	**H**	-2.2709	4.5099	-1.4837
C	9.5258	-4.6693	2.8664	**H**	-3.8144	10.0019	0.5577	**H**	0.7902	3.6759	1.4203
C	9.9483	-4.6312	1.5327	**H**	-2.1675	8.2440	1.0574	**H**	1.3895	6.0442	1.4792

Table S6. Cartesian coordinates [Å] of the optimized structure for **TTT-3TTAC** (**9**).

	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
C	-2.6817	10.2996	-0.5402	**C**	-5.1034	10.8802	-0.1740	**H**	-6.9599	-1.0252	-1.1171
C	-2.8473	8.8964	-0.6119	**C**	-6.1991	11.7233	-0.3333	**H**	-4.9708	0.4603	-1.1927
C	-1.7847	8.0100	-0.4529	**C**	-15.3862	-5.2592	9.5449	**H**	-2.8601	-2.2588	1.3914
C	-0.5189	8.5476	-0.2108	**C**	-14.5766	-6.2073	10.1846	**H**	-4.8216	-3.7428	1.4346
C	-0.3153	9.9493	-0.1557	**C**	-13.6345	-6.9556	9.4800	**H**	10.4010	17.0645	3.2556
C	-1.3985	10.8158	-0.3153	**C**	-13.4868	-6.7856	8.0965	**H**	7.9705	17.2739	2.8687
N	0.7154	7.9034	-0.0400	**C**	-14.2959	-5.8445	7.4428	**H**	8.1771	14.1761	-0.0978

C	1.7070	8.8808	0.1269	**C**	-15.2201	-5.0904	8.1626	**H**	10.6015	13.9492	0.3063
C	3.0731	8.7387	0.3781	**N**	-12.5366	-7.5499	7.3720	**H**	4.1876	16.6041	2.2267
C	3.8296	9.8976	0.5367	**C**	-12.3785	-8.9302	7.6575	**H**	3.1572	18.8446	2.1222
C	3.2606	11.1906	0.4610	**C**	-11.0997	-9.5053	7.7195	**H**	6.4951	20.2720	-0.1723
C	1.8834	11.3076	0.2280	**C**	-10.9513	-10.8618	7.9965	**H**	7.5137	18.0235	-0.0889
C	1.1031	10.1619	0.0617	**C**	-12.0605	-11.6865	8.2382	**H**	3.7773	21.4385	1.8840
C	0.9214	6.5085	-0.0366	**C**	-13.3300	-11.0975	8.1858	**H**	4.8000	21.8448	0.4958
C	1.9197	5.9396	-0.8403	**C**	-13.4947	-9.7439	7.8909	**H**	3.2182	21.0927	0.2450
C	2.1146	4.5638	-0.8382	**C**	-11.8849	-13.1578	8.5290	**H**	12.4961	15.9241	2.9233
C	1.3026	3.7287	-0.0507	**C**	-16.4198	-4.4666	10.3088	**H**	12.4796	14.3217	2.1679
C	0.3091	4.3041	0.7552	**C**	-11.7474	-6.9375	6.3708	**H**	12.7462	15.7608	1.1796
C	0.1259	5.6822	0.7677	**C**	-11.4476	-7.6156	5.1788	**H**	4.4790	15.5712	-0.5831
N	-1.2937	-0.1014	0.1254	**C**	-10.6620	-7.0122	4.2014	**H**	3.0913	13.5591	-0.8775
C	-0.7105	1.1575	0.0576	**C**	-10.1626	-5.7081	4.3606	**H**	5.3455	11.5587	2.1872
N	0.6788	1.2371	0.0724	**C**	-10.4774	-5.0369	5.5547	**H**	6.7424	13.5650	2.4679
C	1.4755	0.1021	-0.0068	**C**	-11.2456	-5.6383	6.5471	**H**	-11.4456	14.2340	0.4595
N	0.8529	-1.1406	0.0648	**C**	-12.3034	-6.9001	-10.8086	**H**	-9.8370	13.9216	-1.3883
C	-0.5310	-1.2635	0.0533	**C**	-13.5999	-6.8684	-10.2768	**H**	-6.5883	14.0682	1.4161
C	1.3060	-2.4646	-0.0479	**C**	-13.8333	-7.0498	-8.9146	**H**	-8.1970	14.3550	3.2659
N	0.2569	-3.2592	-0.1038	**C**	-12.7645	-7.2866	-8.0387	**H**	-6.8475	12.8174	-3.6399
N	-0.9006	-2.5066	-0.0452	**C**	-11.4628	-7.3273	-8.5589	**H**	-7.1771	14.0274	-5.7654
C	1.5918	2.2950	-0.0587	**C**	-11.2426	-7.1261	-9.9202	**H**	-8.2994	17.5524	-3.5841
N	2.8006	1.7882	-0.1866	**N**	-12.9961	-7.4799	-6.6527	**H**	-7.9450	16.3486	-1.4568
N	2.7305	0.4076	-0.1593	**C**	-14.0889	-8.2775	-6.2265	**H**	-8.6378	16.0773	-6.8129
C	-2.6705	0.1652	0.0580	**C**	-14.8862	-7.8770	-5.1431	**H**	-8.3807	17.6186	-5.9794
N	-2.8373	1.4690	-0.0263	**C**	-15.9552	-8.6662	-4.7270	**H**	-7.0094	16.7472	-6.6810
N	-1.6059	2.0966	-0.0317	**C**	-16.2790	-9.8654	-5.3799	**H**	-11.9321	14.2003	2.8601
C	9.1212	-5.7611	-3.2776	**C**	-15.4833	-10.2470	-6.4673	**H**	-10.6239	13.9946	4.0377
C	7.8584	-5.2264	-3.6260	**C**	-14.3980	-9.4755	-6.8835	**H**	-10.9996	15.6003	3.4041
C	6.9330	-4.8142	-2.6701	**C**	-17.4360	-10.7154	-4.9122	**H**	-4.6975	14.2111	-2.0940
C	7.2831	-4.9443	-1.3247	**C**	-12.0601	-6.7268	-12.2887	**H**	-2.7765	12.6913	-1.8498
C	8.5491	-5.4554	-0.9429	**C**	-12.1432	-6.8781	-5.6993	**H**	-5.2264	9.9577	0.3867
C	9.4570	-5.8657	-1.9210	**C**	-11.7773	-7.5639	-4.5302	**H**	-7.1612	11.4496	0.0881
N	6.5699	-4.5909	-0.1703	**C**	-10.9438	-6.9644	-3.5914	**H**	-14.6725	-6.3548	11.2582
C	7.3670	-4.8745	0.9478	**C**	-10.4317	-5.6692	-3.7827	**H**	-13.0100	-7.6768	9.9981

C	7.0852	-4.7366	2.3084	**C**	-10.7990	-4.9970	-4.9615	**H**	-14.1900	-5.7027	6.3717
C	8.0640	-5.1281	3.2187	**C**	-11.6431	-5.5818	-5.9003	**H**	-15.8337	-4.3632	7.6348
C	9.3122	-5.6544	2.8102	**C**	11.7755	-7.0780	-11.4481	**H**	-10.2269	-8.8832	7.5473
C	9.5655	-5.7995	1.4394	**C**	12.4223	-8.2223	-10.9608	**H**	-9.9500	-11.2856	8.0404
C	8.5992	-5.4189	0.5062	**C**	12.7544	-8.3533	-9.6136	**H**	-14.2111	-11.7093	8.3667
C	5.2703	-4.0427	-0.1393	**C**	12.4595	-7.3239	-8.7083	**H**	-14.4891	-9.3106	7.8482
C	4.2295	-4.6561	-0.8506	**C**	11.8184	-6.1712	-9.1839	**H**	-11.1273	-13.3258	9.3042
C	2.9533	-4.1074	-0.8281	**C**	11.4757	-6.0615	-10.5305	**H**	-12.8214	-13.6103	8.8714
C	2.6892	-2.9415	-0.0871	**N**	12.8022	-7.4480	-7.3375	**H**	-11.5597	-13.7060	7.6348
C	3.7311	-2.3419	0.6360	**C**	14.0575	-7.9984	-6.9729	**H**	-16.1779	-4.4204	11.3761
C	5.0119	-2.8830	0.6024	**C**	14.1582	-8.9053	-5.9072	**H**	-16.4944	-3.4392	9.9347
C	-9.3410	-5.0669	3.3080	**C**	15.3948	-9.4395	-5.5525	**H**	-17.4167	-4.9192	10.2176
C	-8.2450	-4.2423	3.6540	**C**	16.5647	-9.1065	-6.2510	**H**	-11.8219	-8.6234	5.0299
C	-7.4445	-3.6240	2.6962	**C**	16.4481	-8.2107	-7.3219	**H**	-10.4218	-7.5698	3.3003
C	-7.7473	-3.8457	1.3513	**C**	15.2197	-7.6539	-7.6763	**H**	-10.1255	-4.0201	5.7059
C	-8.8491	-4.6533	0.9716	**C**	17.9029	-9.6755	-5.8444	**H**	-11.4734	-5.0979	7.4603
C	-9.6373	-5.2593	1.9517	**C**	11.4409	-6.9333	-12.9133	**H**	-14.4444	-6.6836	-10.9374
N	-7.1406	-3.3340	0.1954	**C**	11.8937	-7.0304	-6.3378	**H**	-14.8448	-7.0100	-8.5225
C	-7.8450	-3.8059	-0.9214	**C**	12.3510	-6.3864	-5.1771	**H**	-10.6269	-7.5090	-7.8906
C	-7.6032	-3.6096	-2.2825	**C**	11.4539	-5.9842	-4.1928	**H**	-10.2238	-7.1579	-10.3007
C	-8.4586	-4.2281	-3.1910	**C**	10.0703	-6.1931	-4.3285	**H**	-14.6609	-6.9465	-4.6312
C	-9.5439	-5.0378	-2.7803	**C**	9.6250	-6.8310	-5.4994	**H**	-16.5604	-8.3350	-3.8855
C	-9.7554	-5.2352	-1.4090	**C**	10.5149	-7.2499	-6.4837	**H**	-15.7065	-11.1720	-6.9944
C	-8.9099	-4.6296	-0.4774	**C**	12.4383	-6.7701	10.8419	**H**	-13.7904	-9.7950	-7.7244
C	-6.0169	-2.4816	0.1617	**C**	13.6884	-6.4273	10.3089	**H**	-18.3445	-10.1162	-4.7757
C	-6.0543	-1.2951	-0.5842	**C**	13.9589	-6.5520	8.9471	**H**	-17.6627	-11.5094	-5.6314
C	-4.9420	-0.4636	-0.6251	**C**	12.9794	-7.0440	8.0730	**H**	-17.2166	-11.1942	-3.9486
C	-3.7747	-0.7953	0.0858	**C**	11.7263	-7.3968	8.5945	**H**	-12.8480	-6.1252	-12.7552
C	-3.7494	-1.9754	0.8437	**C**	11.4638	-7.2497	9.9552	**H**	-11.1003	-6.2349	-12.4821
C	-4.8578	-2.8151	0.8737	**N**	13.2509	-7.1809	6.6876	**H**	-12.0398	-7.6961	-12.8055
C	10.6914	15.4925	1.8111	**C**	14.5046	-7.6905	6.2631	**H**	-12.1432	-8.5727	-4.3675
C	9.9221	16.4271	2.5155	**C**	15.1809	-7.1125	5.1779	**H**	-10.6521	-7.5291	-2.7100
C	8.5487	16.5493	2.3038	**C**	16.4102	-7.6198	4.7642	**H**	-10.4506	-3.9814	-5.1283
C	7.9045	15.7414	1.3578	**C**	17.0153	-8.7017	5.4210	**H**	-11.9275	-5.0332	-6.7926
C	8.6652	14.8066	0.6390	**C**	16.3361	-9.2608	6.5113	**H**	12.6585	-9.0349	-11.6446

C	10.0322	14.6828	0.8738	**C**	15.0959	-8.7749	6.9249	**H**	13.2448	-9.2533	-9.2557
N	6.5103	15.8673	1.1288	**C**	18.3400	-9.2540	4.9518	**H**	11.5838	-5.3677	-8.4926
C	5.9202	17.1560	1.0703	**C**	12.1598	-6.6553	12.3215	**H**	10.9748	-5.1596	-10.8761
C	4.6883	17.4068	1.6944	**C**	12.2781	-6.8052	5.7329	**H**	13.2633	-9.1872	-5.3610
C	4.1123	18.6729	1.6298	**C**	12.0878	-7.5629	4.5664	**H**	15.4484	-10.1429	-4.7241
C	4.7446	19.7329	0.9623	**C**	11.1345	-7.1849	3.6264	**H**	17.3362	-7.9318	-7.8849
C	5.9793	19.4724	0.3548	**C**	10.3258	-6.0503	3.8140	**H**	15.1542	-6.9564	-8.5056
C	6.5592	18.2042	0.3956	**C**	10.5207	-5.3053	4.9901	**H**	17.8156	-10.7238	-5.5363
C	4.1042	21.0987	0.8937	**C**	11.4809	-5.6667	5.9301	**H**	18.6247	-9.6246	-6.6666
C	12.1796	15.3681	2.0345	**H**	-3.8332	8.4945	-0.8258	**H**	18.3306	-9.1224	-4.9970
C	5.7108	14.7132	0.9635	**H**	-1.9427	6.9399	-0.5360	**H**	11.2541	-7.9075	-13.3787
C	4.6640	14.6936	0.0282	**H**	-1.2502	11.8897	-0.2440	**H**	10.5508	-6.3119	-13.0613
C	3.8757	13.5576	-0.1255	**H**	3.5404	7.7622	0.4475	**H**	12.2648	-6.4604	-13.4654
C	4.1040	12.3954	0.6318	**H**	4.8988	9.8034	0.7014	**H**	13.4127	-6.1956	-5.0567
C	5.1602	12.4257	1.5589	**H**	1.4182	12.2891	0.2096	**H**	11.8318	-5.4609	-3.3186
C	5.9459	13.5611	1.7306	**H**	2.5209	6.5768	-1.4801	**H**	8.5661	-7.0402	-5.6245
C	-9.9474	14.3235	2.0062	**H**	2.8855	4.1195	-1.4586	**H**	10.1468	-7.7582	-7.3692
C	-10.3805	14.2028	0.6791	**H**	-0.3190	3.6836	1.3812	**H**	14.4629	-6.0410	10.9681
C	-9.4782	14.0242	-0.3688	**H**	-0.6259	6.1252	1.4120	**H**	14.9307	-6.2698	8.5540
C	-8.1003	13.9776	-0.1161	**H**	7.6118	-5.1057	-4.6766	**H**	10.9594	-7.7781	7.9275
C	-7.6531	14.1041	1.2074	**H**	5.9826	-4.3865	-2.9711	**H**	10.4830	-7.5260	10.3367
C	-8.5670	14.2634	2.2468	**H**	10.4157	-6.2859	-1.6302	**H**	14.7369	-6.2661	4.6631
N	-7.1764	13.8047	-1.1782	**H**	6.1297	-4.3576	2.6551	**H**	16.9175	-7.1541	3.9217
C	-7.3688	14.5005	-2.3990	**H**	7.8491	-5.0525	4.2805	**H**	16.7778	-10.1010	7.0426
C	-7.1591	13.8572	-3.6289	**H**	10.5223	-6.1883	1.1026	**H**	14.5845	-9.2283	7.7682
C	-7.3453	14.5468	-4.8240	**H**	4.4241	-5.5675	-1.4060	**H**	19.0378	-8.4510	4.6870
C	-7.7619	15.8868	-4.8403	**H**	2.1433	-4.5852	-1.3685	**H**	18.8121	-9.8690	5.7254
C	-7.9789	16.5132	-3.6068	**H**	3.5569	-1.4386	1.2058	**H**	18.2166	-9.8836	4.0602
C	-7.7782	15.8401	-2.4013	**H**	5.8212	-2.3970	1.1366	**H**	12.7858	-5.8862	12.7871
C	-7.9590	16.6217	-6.1446	**H**	-8.0037	-4.1033	4.7036	**H**	11.1117	-6.3996	12.5134
C	-10.9270	14.5376	3.1352	**H**	-6.6139	-2.9938	2.9955	**H**	12.3646	-7.6019	12.8402
C	-6.0683	12.9396	-1.0216	**H**	-10.4994	-5.8546	1.6644	**H**	12.6857	-8.4546	4.4067
C	-4.8135	13.2778	-1.5523	**H**	-6.7658	-3.0142	-2.6307	**H**	10.9871	-7.8062	2.7472
C	-3.7292	12.4182	-1.4046	**H**	-8.2672	-4.1072	-4.2531	**H**	9.9383	-4.4027	5.1538
C	-3.8438	11.2028	-0.7079	**H**	-10.5907	-5.8417	-1.0706	**H**	11.6250	-5.0627	6.8203

Crystallographic Data

Table S7. X-ray diffraction collection data for **TTT-3HMAT** (**5**) and refinement details (Cambridge Crystallographic Data Centre deposit number: 2099446).

Compound	**TTT-3HMAT**
Formula	$C_{110.97}H_{105.8}N_{12}$
$D_{calc.}$/ g cm^{-3}	1.195
μ/mm^{-1}	0.071
Formula Weight	1607.57
Colour	colourless
Shape	prism
Size/mm^3	0.26×0.20×0.18
T/K	133(2)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	35.516(3)
b/Å	21.2544(18)
c/Å	23.778(2)
α/°	90
β/°	95.152(3)
γ/°	90
V/Å^3	17877(3)
Z	8
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	1.118
Θ_{max}/°	25.430
Measured Refl's.	88016
Indep't Refl's	16436
Refl's I≥2σ(I)	12120
R_{int}	0.0478
Parameters	1499
Restraints	3420
Largest Peak	0.777
Deepest Hole	-0.419
GooF	1.038
wR_2 (all data)	0.1974
wR_2	0.1772
R_1 (all data)	0.0876
R_1	0.0637

X-ray Crystallography Methods

Single colourless prism crystals of **TTT-3HMAT** recrystallised from a mixture of benzene and heptane by slow evaporation. A suitable crystal with dimensions 0.26 × 0.20 × 0.18 mm^3 was selected and mounted on a MITIGEN holder in oil on a Bruker APEX II area detector diffractometer. The crystal was kept at a steady T = 133(2) K during data collection. The structure was solved with the **XT** solution program

using Intrinsic Phasing methods and by using Olex2 as the graphical interface.[4] The model was refined with **XL** using full matrix least squares minimisation on $\boldsymbol{F^2}$.[5]

Crystal Data. $C_{110.97}H_{105.8}N_{12}$, M_r = 1607.57, monoclinic, *C*2/*c* (No. 15), a = 35.516(3) Å, b = 21.2544(18) Å, c = 23.778(2) Å, β = 95.152(3)°, $\alpha = \gamma = 90°$, V = 17877(3) Å^3, T = 133(2) K, Z = 8, Z' = 1, μ (MoK$_\alpha$) = 0.071, 88016 reflections measured, 16436 unique (R_{int} = 0.0478) which were used in all calculations. The final wR_2 was 0.1974 (all data) and R_1 was 0.0637 (I≥2 σ(I)). A colourless prism-shaped crystal with dimensions 0.26 × 0.20 × 0.18 mm^3 was mounted on a MITIGEN holder in oil. Data were collected using a Bruker APEX II area detector diffractometer equipped with a Kryoflex low-temperature device operating at T = 133(2) K. Data were measured using ϕ and ω scans of 0.5 ° per frame for 30 s using MoK$_\alpha$ radiation (microfocus sealed X-ray tube, 50 kV, 0.99 mA). The total number of runs and images was based on the strategy calculation from the program APEX3. The maximum resolution that was achieved was Θ = 25.430° (0.83 Å). The unit cell was refined using SAINT on 9777 reflections, 11% of the observed reflections.[6] Data reduction, scaling and absorption corrections were performed using SAINT The final completeness is 100.00 % out to 25.430° in Θ.[6] A multi-scan absorption correction was performed using SADABS-2016/2 was used for absorption correction.[7] wR_2(int) was 0.1091 before and 0.0521 after correction. The ratio of minimum to maximum transmission is 0.8502. The λ/2 correction factor is not present. The absorption coefficient μ of this material is 0.071 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.839 and 0.987.

The structure was solved, and the space group *C*2/*c* (# 15) determined by the **XT** structure solution program using Intrinsic Phasing methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2018/3 of **XL**.[5,8] There is a considerable amount of disorder in the structure. Two of the three fused-ring system about the outside of the molecule are disordered and were modeled with distance restraints. Additionally, a significant amount of solvent crystallizes in the lattice as well. Both benzene and heptane are found in the lattice, some in fully occupied sites, others only partially occupied, with occupancies determined by refining the site occupancies. Restraints were employed to maintain reasonable bond lengths and angles for the benzene molecules. The fully and near-fully occupied benzene rings were refined with anisotropic displacement parameters. All other benzene atoms were refined isotropically, with displacement parameters fixed at the values suggested by the Wilson plot. All other non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

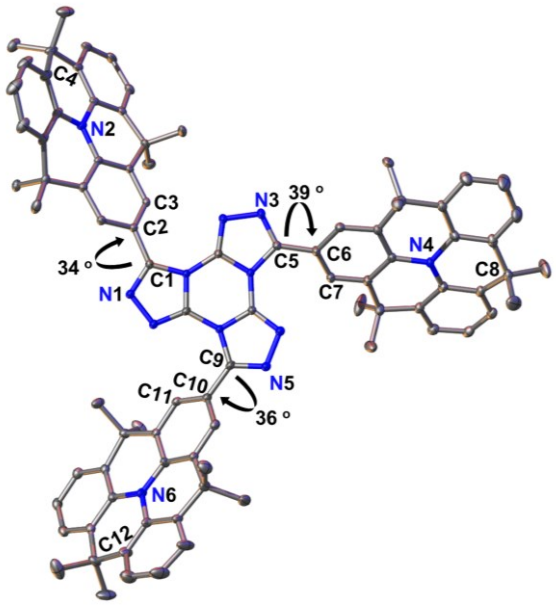


Figure S35. Crystal structure of **TTT-3HMAT (5)**.

Table S8. Selected angles of **TTT-3HMAT**.

Selected atom	Dihedral (º)	Selected atom	Bowl (º)
N1-C1-C2-C3	34.11	C2-N2-C4	172.43
N3-C5-C6-C7	39.22	C6-N4-C8	174.43
N5-C9-C10-C11	36.31	C10-N6-C12	179.19

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