Supporting Information for

Deep Blue Emission and Thermally Activated Delayed Fluorescence via Dimroth Rearrangement of Tris(triazolo)triazines

By Ryoga Hojo, Don M. Mayder, and Zachary M. Hudson*

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada, V6T 1Z1.
Tel: +1-604-822-3266; Fax: +1-604-822-2847; e-mail: zhudson@chem.ubc.ca.

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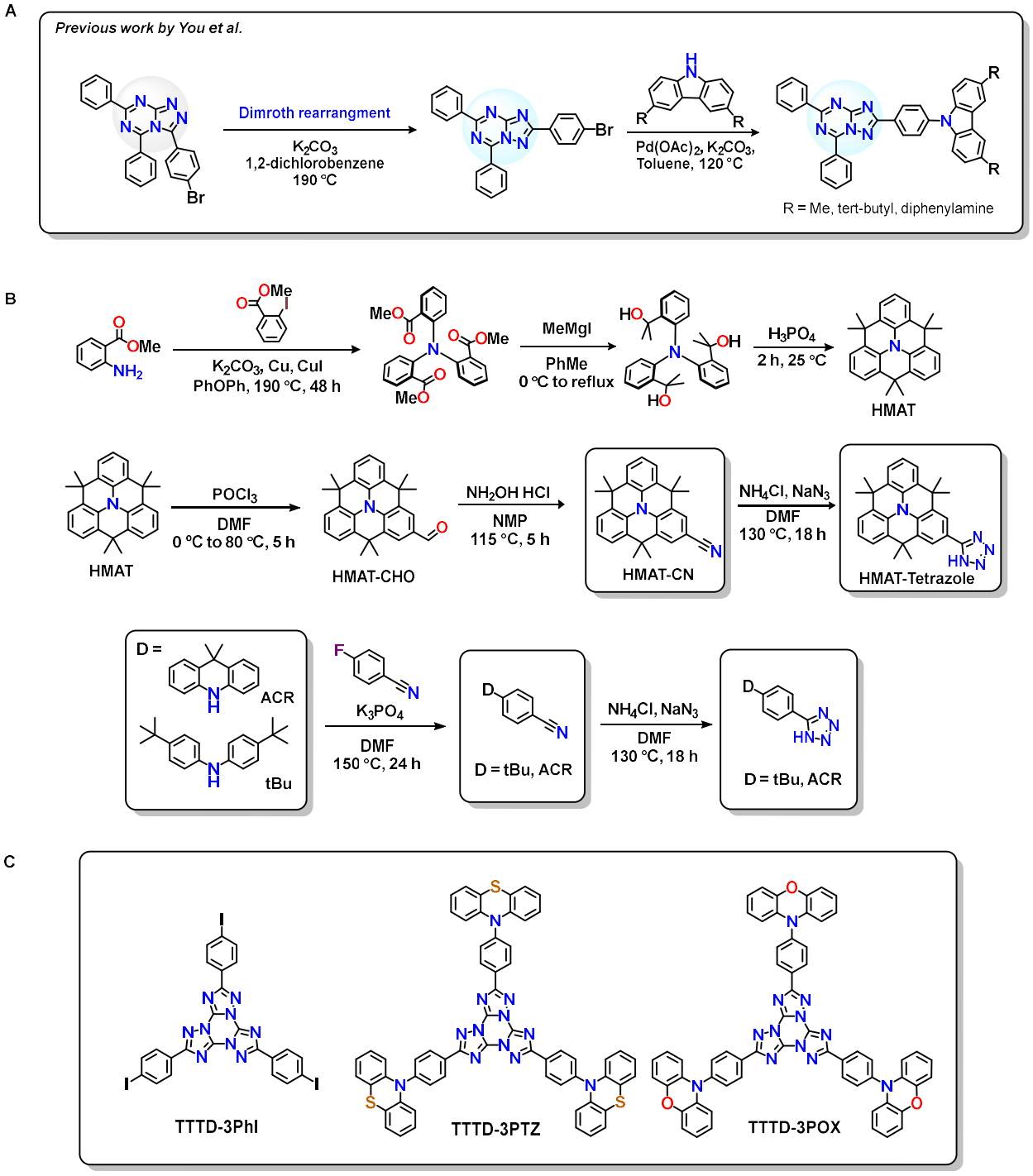
Additional Schemes



Scheme S1. (A) Previous report by the You group exploiting the Dimroth rearrangement on mono-fused (triazolo)triazine derivatives.[1] (B) Synthetic route for donor-appended aryl nitriles and subsequent conversion to tetrazoles.[2–5] (C) Attempted synthesis and characterization of TTTD derivatives containing the pre-assembled TTTD core (TTTD-3PhI), 10*H*-phenoxazine (TTTD-3PTZ) or 10*H*-phenothiazine donors (TTTD-POX).

General procedure for the attempted syntheses of **TTTD-3PhI**, **TTTD-3PTZ**, *and* **TTTD-3POX**: TTT-precursor starting material (0.39 mmol, 1.0 eq) was added to a 100 mL Schlenk flask equipped with magnetic stir bar. K2CO3 (0.22 g, 1.6 mmol, 4.0 eq) was added, and the mixture was suspended in anhydrous 1,2-dichlorobenzene (50 mL). The reaction mixture was sparged for 15 minutes with N_2 before being heated to 200 °C for 3 to 4 days. Upon cooling, n-hexane (60 mL) was added to fully precipitate all solids that were then collected by vacuum filtration, and washed with a mixture of 9:1 EtOAc:*n*-hexane (20 mL). The solid product was suspended in water (30 mL) and sonicated to dissolve inorganic salts, before being filtered again and washed with water (10 mL) and cold ethanol (20 mL). The solids were dried in vacuo, but could not be characterized by ^{1}H NMR due to insufficient signal to noise resulting from limited solubility (attempted NMR solvents include C_6D_6, CD_2Cl_2, $CDCl_3$, TFA-d_1, DMSO-d_6, THF-d_8, and pyridine-d_5).

^{1}H and $^{13}C\{^{1}H\}$ NMR Spectroscopy

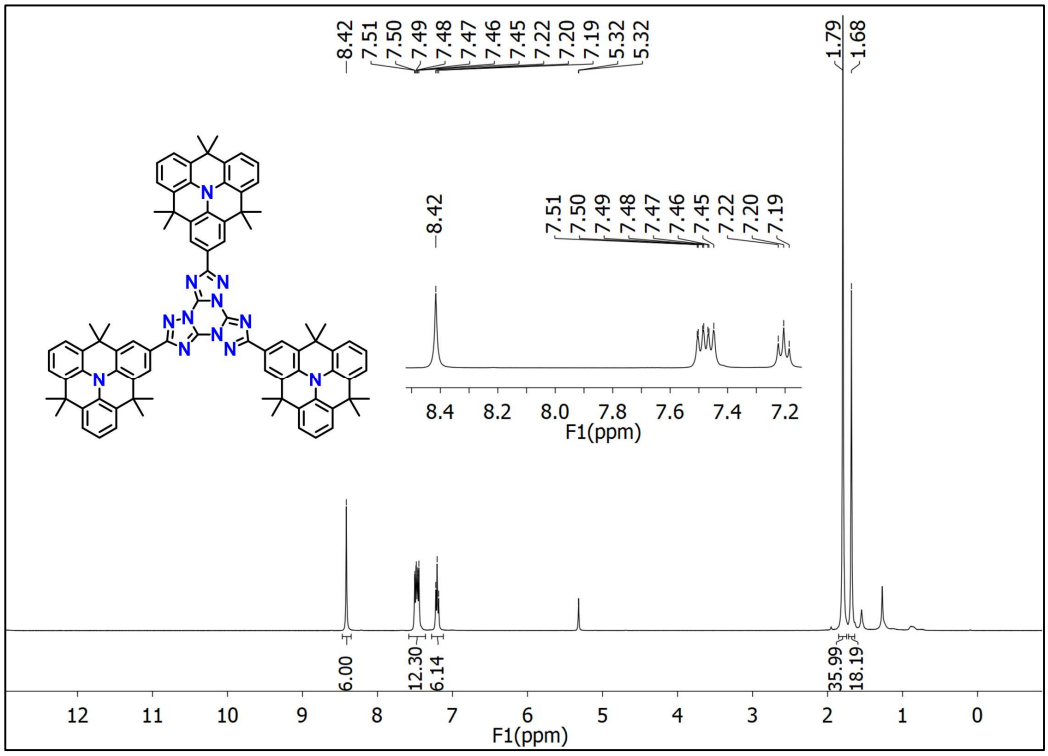


Figure S1A. ^{1}H NMR (300 MHz) of **TTTD-3HMAT** in CD_2Cl_2.

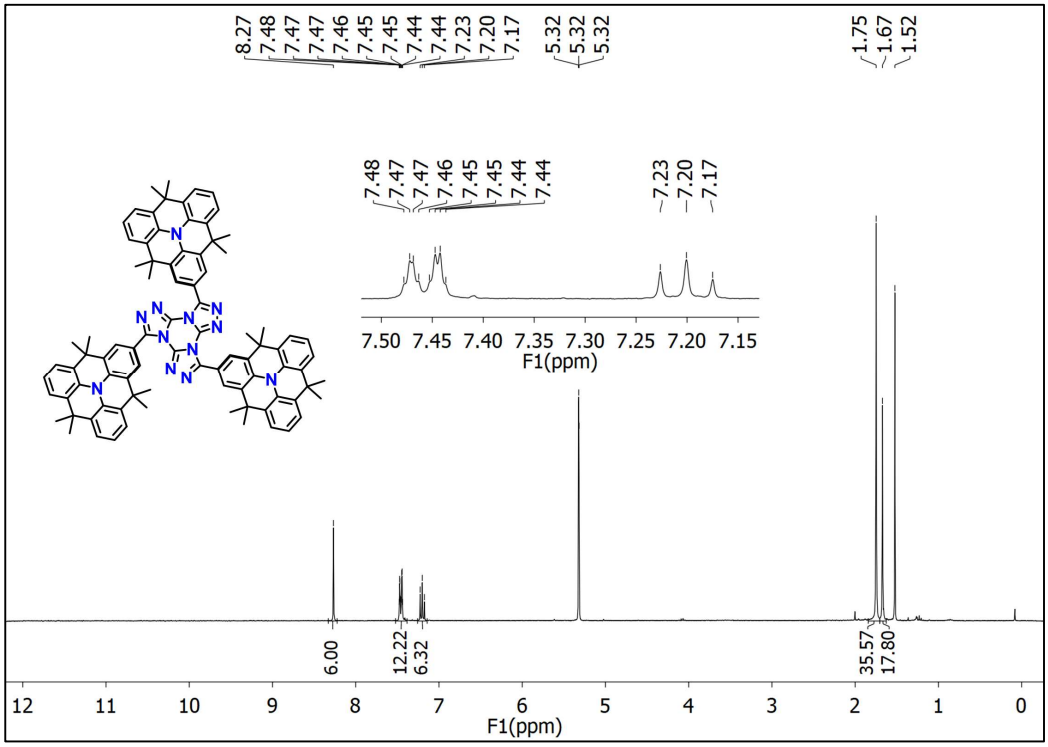


Figure S1B. ^{1}H NMR (300 MHz) of TTT-3HMAT in CD_2Cl_2.

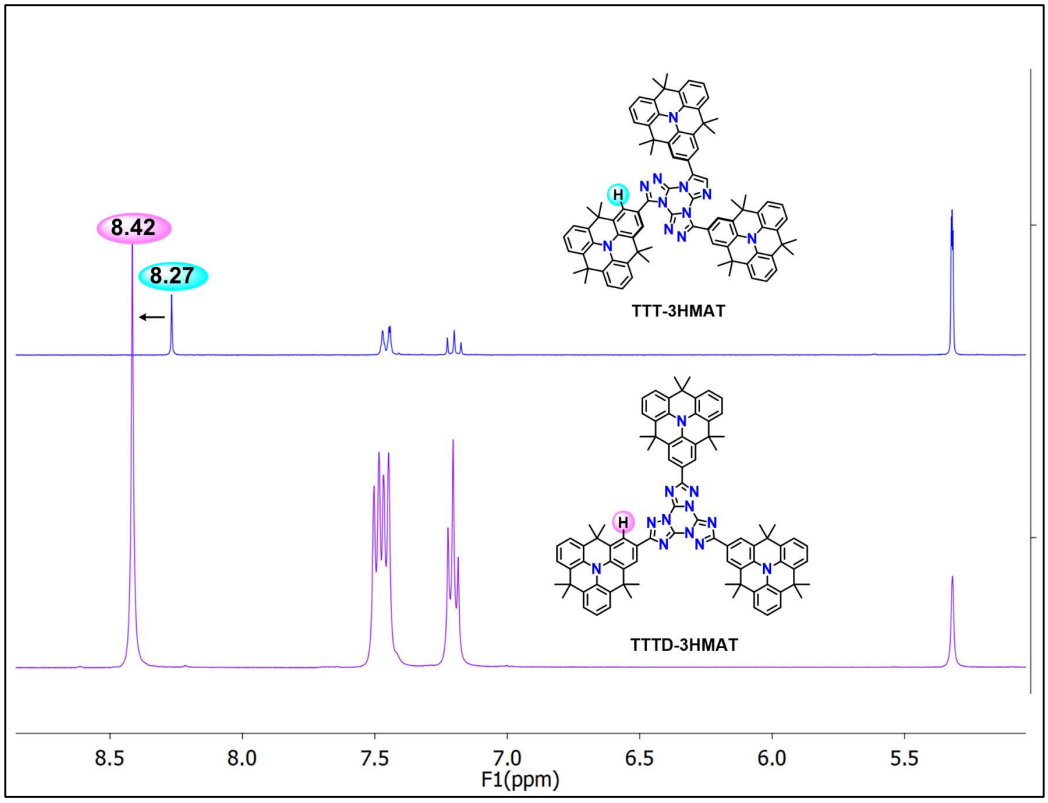


Figure S1C. Singlet aromatic shift showing the isomer conversion from TTT-3HMAT to **TTTD-3HMAT**: ^{1}H NMR (300 MHz) in CD_2Cl_2.

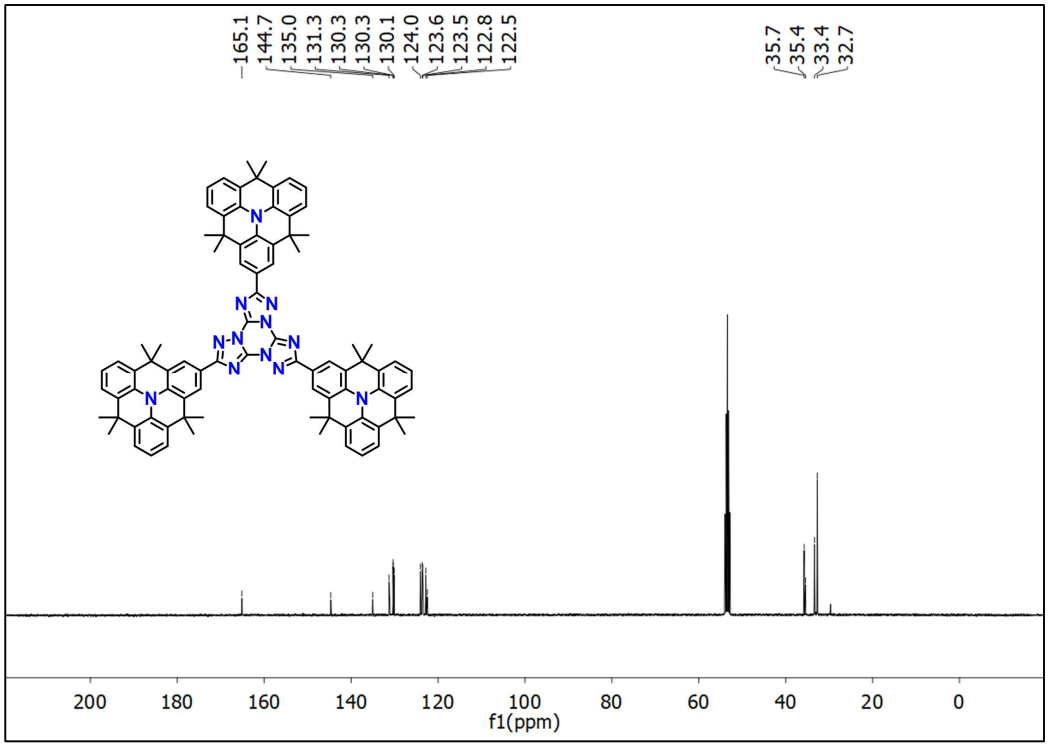


Figure S2. $^{13}C\{^{1}H\}$ NMR (101 MHz) of **TTTD-3HMAT** in CD_2Cl_2.

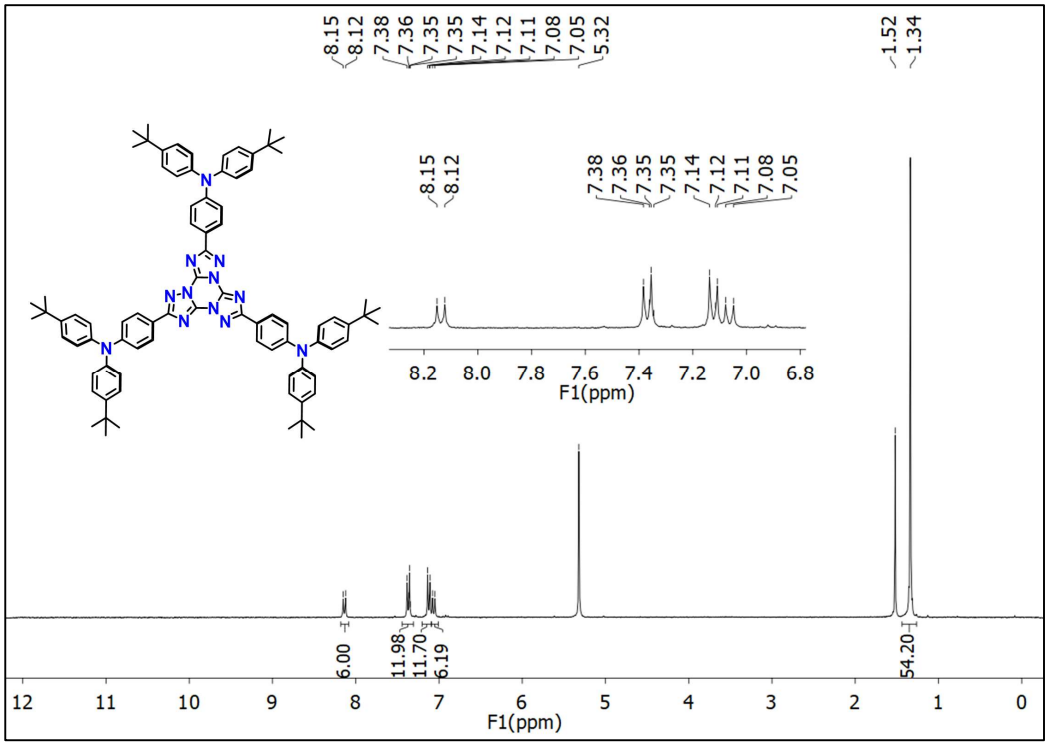


Figure S3. ^{1}H NMR (300 MHz) of **TTTD-3tBu** in CD_2Cl_2.

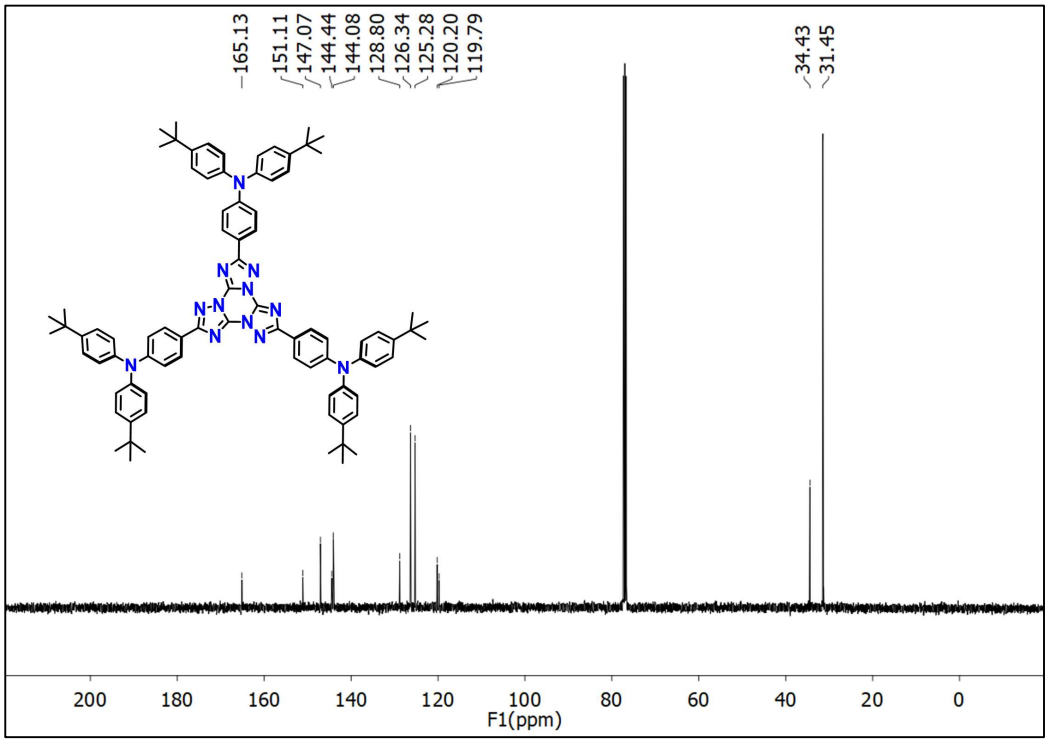


Figure S4. ^{13}C{^{1}H} NMR (101 MHz) of **TTTD-3tBu** in $CDCl_3$.

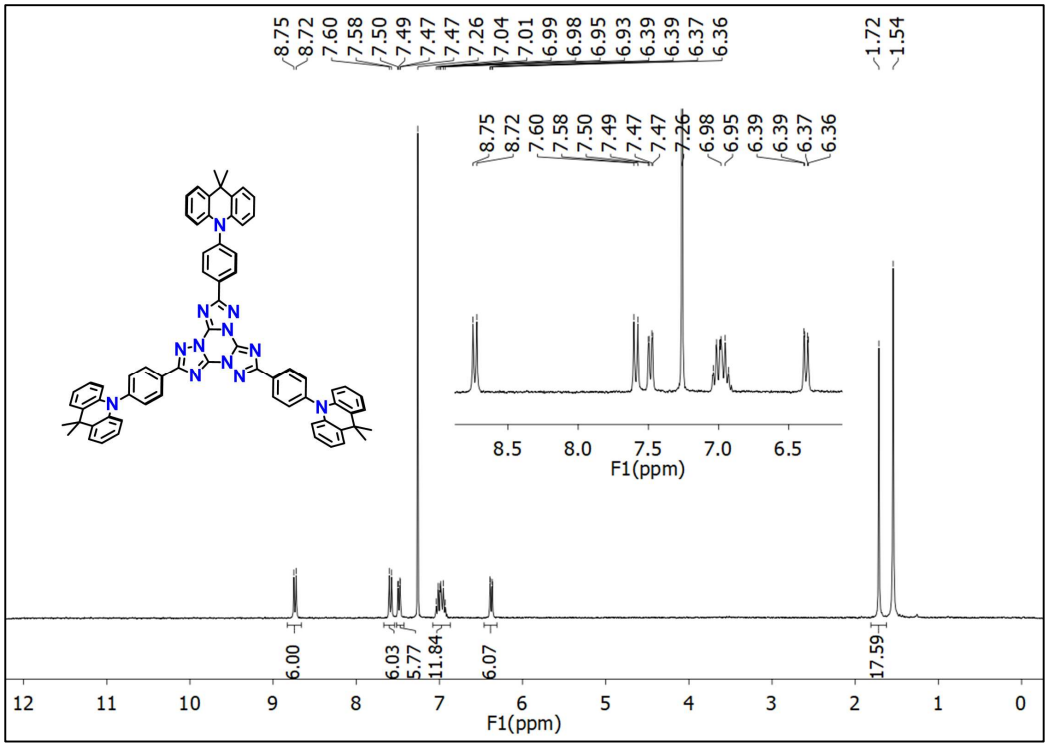


Figure S5. ^{1}H NMR (300 MHz) of **TTTD-3ACR** in $CDCl_3$.

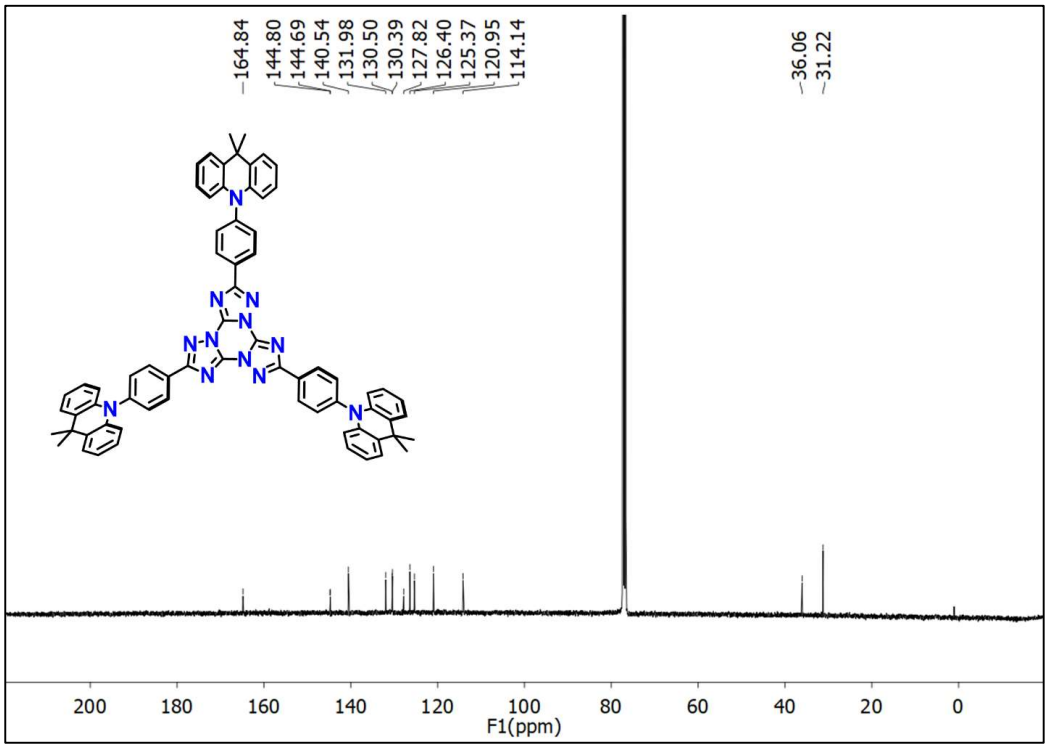


Figure S6. ^{13}C{^{1}H} NMR (101 MHz) of **TTTD-3ACR** in $CDCl_3$.

Photophysical and Electrochemical Characterization

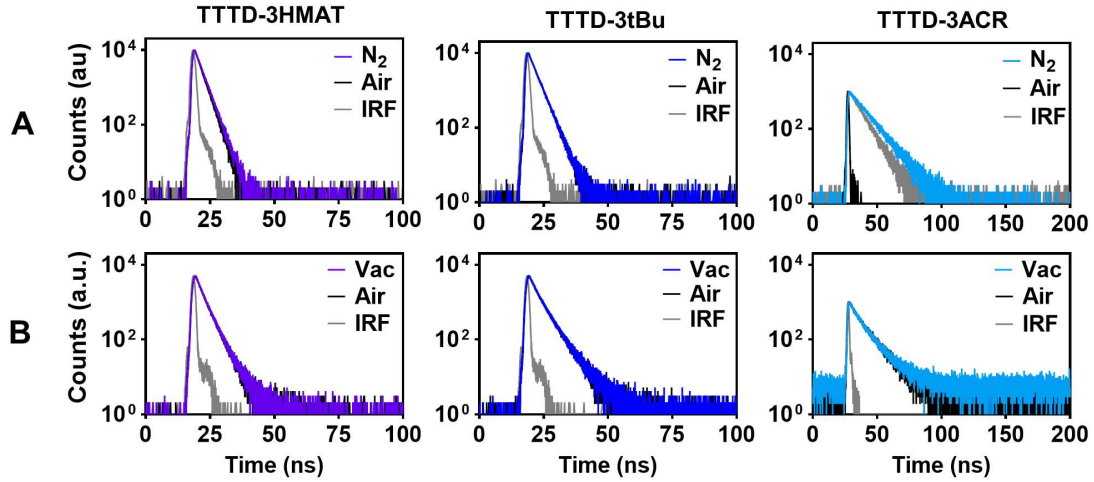


Figure S7. PL decays for (A) toluene solutions at 1 x 10^{-2} mg mL^{-1} under air (black trace) or N_2 (colored trace) and (B) 3 wt.% doped PMMA films under air (black trace) or vacuum (colored trace). All measurements were performed using TCSPC with a 313 nm EPLED source.

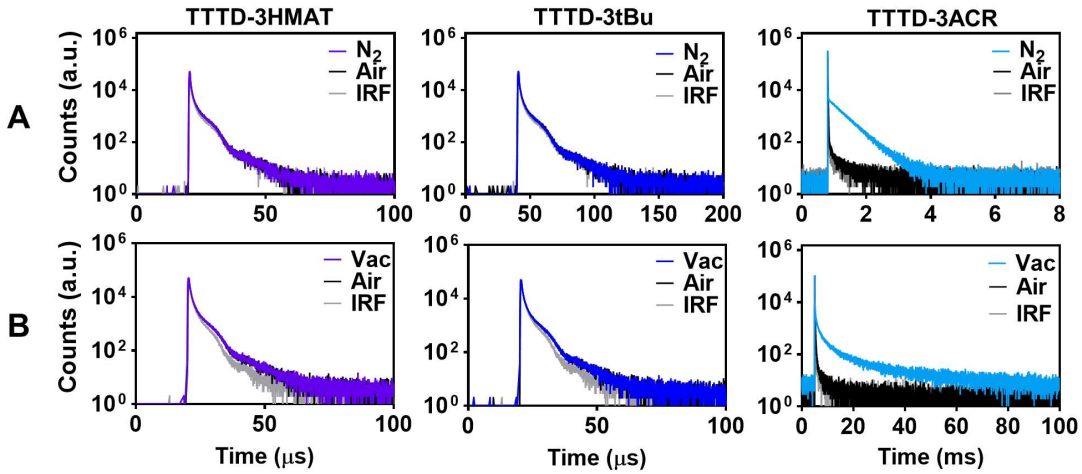


Figure S8. PL decays for (A) toluene solutions at 1 x 10^{-2} mg mL^{-1} under air (black trace) or N_2 (colored trace) and (B) 3 wt.% doped PMMA films under air (black trace) or vacuum (colored trace). All measurements were performed using TCSPC with a 313 nm EPLED source. All measurements were performed using MCS with a 313 nm Xe μF source.

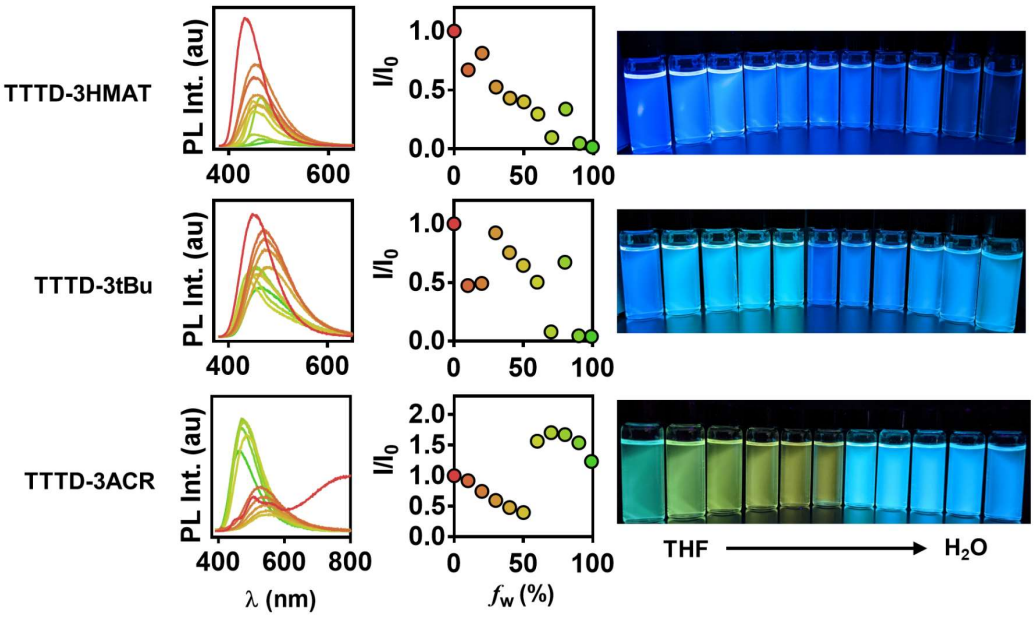


Figure S9. Emission spectra (left column), and relative emission intensity (I/I_0) as a function of water fraction f_w (middle column) for solutions of the three emitters in THF/water solutions ranging from 0% (red) to 99% (green) water. Samples were prepared as 1 x 10^{-2} mg mL^{-1} solutions and were excited at 350 nm. Photographs of the solutions under 365 nm excitation (right column).

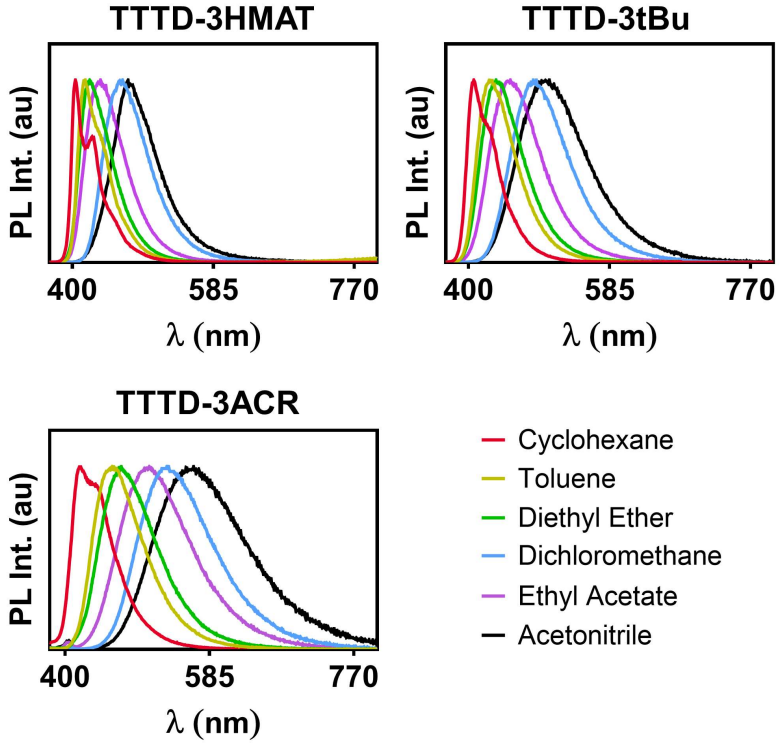


Figure S10. Normalized emission spectra showing solvatochromic shifts, measured at concentrations of 1.0 x 10^{-2} mg mL^{-1}, and excited at 360 nm.

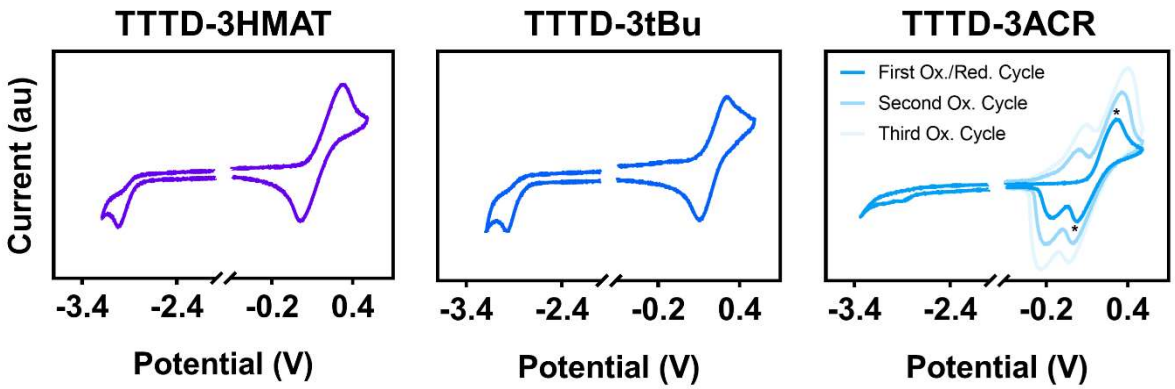


Figure S11. Cyclic voltammograms measured at 2 mg/mL in degassed *o*-difluorobenzene relative to $Fc^{0/+}$, with 0.02 M tetrabutylammonium hexafluorophosphate. The third oxidative and reductive cycles are shown for **TTTD-3HMAT** and **TTTD-3tBu**. For **TTTD-3ACR**, the first oxidative cycle was used, with the annotated (*) oxidation used for the calculation of E_{HOMO}.

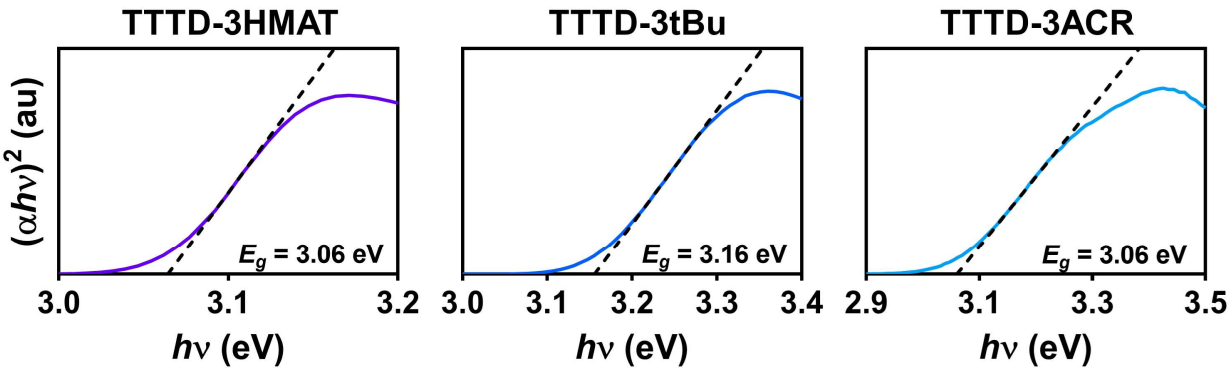


Figure S12. Tauc plots of each compound, with calculated optical gaps (E_g) displayed inset.

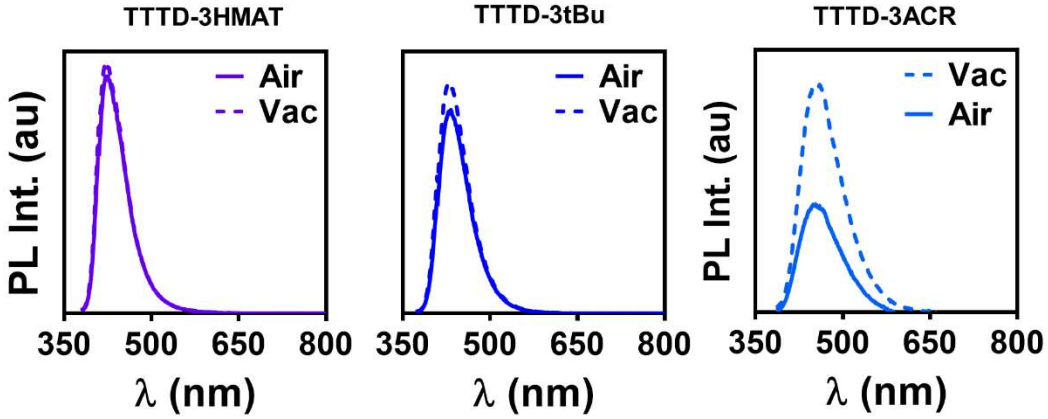


Figure S13. Emission spectra measured in 3 wt.% doped PMMA films under air (solid trace) compared to vacuum (dashed trace) with 350 nm excitation.

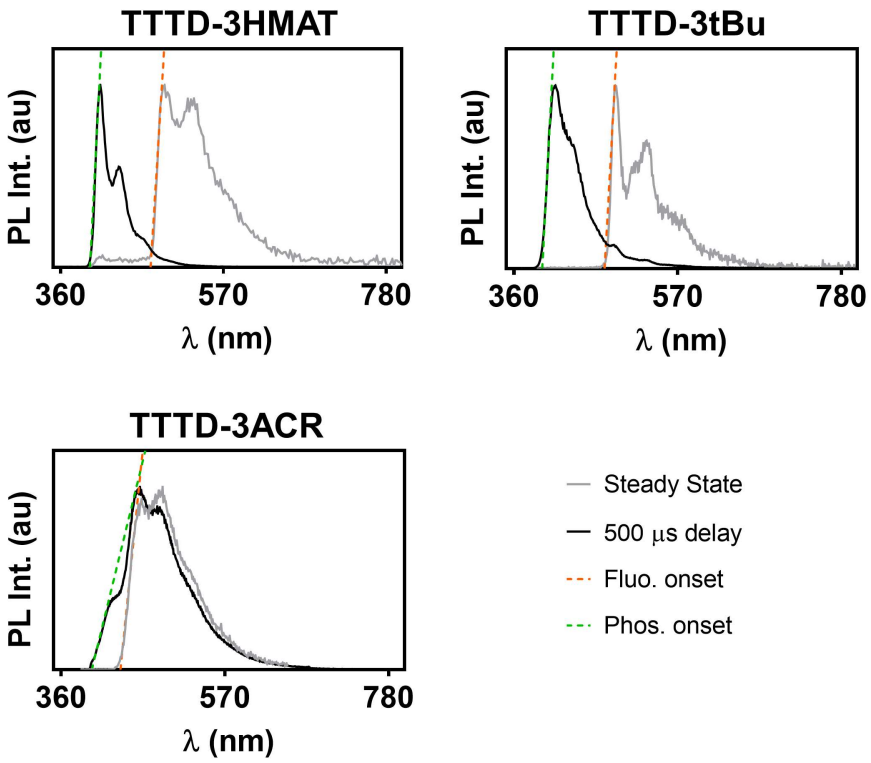


Figure S14. Time-resolved and steady-state emission (no delay = black trace; delayed = grey dashed trace, steady state colored) spectra measured in 2-methyltetrahydrofuran at 77 K.

Density Functional Theory

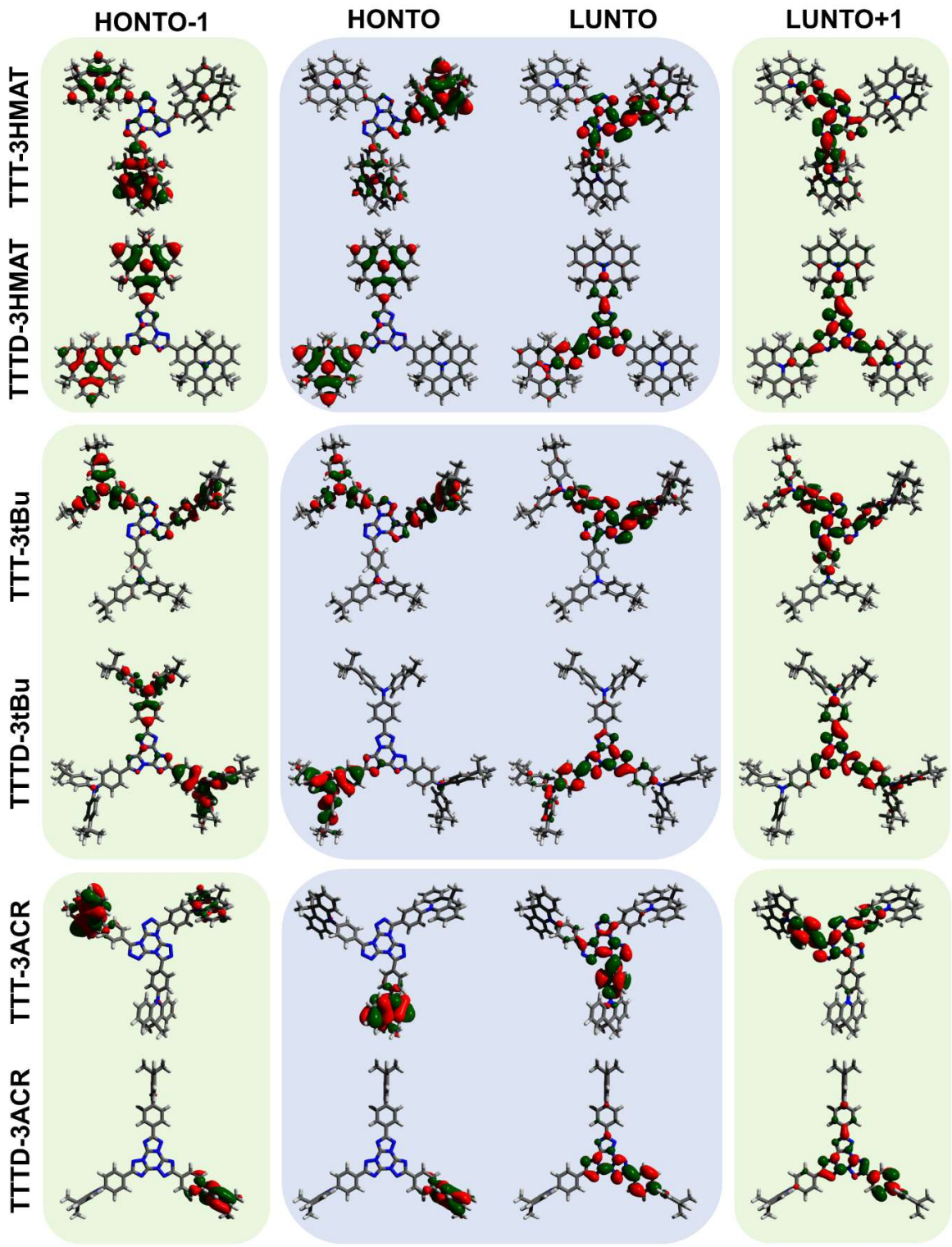


Figure S15. Highest-occupied natural transition orbitals (HONTOs) and lowest-unoccupied natural transition orbitals (LUNTOs) for TTT- and TTTD- compounds.

Table S1. Results of DFT and TDA-DFT calculations.

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)
TTT-3HMAT	-4.90	-1.60	3.30	2.87	0.752	0	-4.02
TTTD-3HMAT	-4.89	-1.58	3.31	2.93	0.878	0	-4.02
TTT-3tBu	-4.98	-1.49	3.49	3.06	0.982	0	-3.91
TTTD-3tBu	-4.95	-1.54	3.42	3.03	1.218	0	-3.91
TTT-3ACR	-5.01	-1.97	3.03	2.54	0.0008	0	-3.32
TTTD-3ACR	-5.00	-1.99	3.01	2.55	0	0	-3.32

[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**.

	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 **TTTD-3HMAT**.

	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
N	-0.6961	-1.1606	0.0002	**C**	-6.5168	-3.6521	0.0000	**H**	4.4492	7.2965	1.2997
C	-1.4007	0.0275	0.0002	**C**	-6.4645	-2.2377	0.0002	**H**	3.5283	5.7883	-1.2986
N	-0.6571	1.1831	0.0002	**C**	-5.2336	-1.5883	0.0002	**H**	2.9088	7.2020	-2.1701
C	0.7242	1.1992	0.0002	**C**	-4.0292	-2.2842	0.0001	**H**	4.4493	7.2965	-1.2993
N	1.3532	-0.0226	0.0002	**C**	-4.0865	-3.6754	-0.0001	**H**	-4.2622	7.4796	-1.3004
C	0.6765	-1.2268	0.0002	**C**	-5.2928	-4.3664	-0.0001	**H**	-2.7268	7.3188	-2.1704
N	2.6996	-0.2679	0.0002	**C**	-5.2069	-5.8823	-0.0003	**H**	-3.4069	5.9333	-1.2990
C	2.7421	-1.6002	0.0001	**C**	-4.4424	-6.3421	1.2690	**H**	-12.3309	-1.5687	0.0004
N	1.5086	-2.2317	0.0001	**C**	-7.6979	-1.3525	0.0003	**H**	-10.1512	-0.4000	0.0005
N	-1.1179	2.4719	0.0002	**C**	-7.6761	-0.4608	1.2697	**H**	-12.3533	-4.0407	0.0002
C	0.0147	3.1748	0.0001	**C**	-7.6762	-0.4606	-1.2689	**H**	-5.7166	-8.4642	-0.0006
N	1.1784	2.4223	0.0001	**C**	-4.4425	-6.3417	-1.2699	**H**	-7.8708	-9.6788	-0.0006
N	-1.5818	-2.2041	0.0002	**C**	7.5459	-8.8092	0.0000	**H**	-9.9704	-8.3736	-0.0004
C	-2.7568	-1.5747	0.0002	**C**	6.3737	-8.0713	0.0000	**H**	-10.6066	-5.9021	2.1700
N	-2.6870	-0.1906	0.0002	**C**	6.3754	-6.6746	0.0000	**H**	-12.1421	-5.7384	1.3007
C	3.8561	10.9395	0.0000	**C**	7.6034	-5.9756	0.0000	**H**	-11.2908	-7.2864	1.3006
C	3.8031	9.5553	0.0001	**C**	8.8019	-6.7231	0.0000	**H**	-11.2909	-7.2861	-1.3009
C	2.5926	8.8585	0.0000	**C**	8.7467	-8.1193	0.0000	**H**	-12.1422	-5.7381	-1.3007
C	1.3734	9.5725	0.0000	**N**	7.6320	-4.5499	0.0000	**H**	-10.6069	-5.9017	-2.1701
C	1.4215	10.9842	-0.0001	**C**	8.8819	-3.8637	0.0000	**H**	-5.1965	-0.5063	0.0004
C	2.6582	11.6344	0.0000	**C**	10.0998	-4.5792	0.0000	**H**	-3.1545	-4.2270	-0.0001
N	0.1244	8.8844	-0.0001	**C**	10.1839	-6.0949	0.0000	**H**	-4.9747	-6.0213	2.1699
C	-1.0948	9.6238	-0.0001	**C**	8.9320	-2.4517	-0.0001	**H**	-4.3463	-7.4312	1.2996
C	-1.0842	11.0363	-0.0002	**C**	10.1688	-1.8027	-0.0001	**H**	-3.4349	-5.9173	1.2984
C	0.1865	11.8669	-0.0001	**C**	11.3660	-2.4993	-0.0001	**H**	-7.6915	-1.0823	2.1705
C	-2.3427	8.9612	-0.0002	**C**	11.3113	-3.8831	-0.0001	**H**	-6.7770	0.1612	1.2993
C	-3.5232	9.7078	-0.0002	**C**	10.9470	-6.5568	1.2697	**H**	-8.5436	0.2048	1.3000
C	-3.5185	11.0929	-0.0003	**C**	10.9470	-6.5569	-1.2698	**H**	-8.5436	0.2050	-1.2991
C	-2.2927	11.7374	-0.0002	**C**	6.4212	-3.8176	0.0000	**H**	-6.7770	0.1615	-1.2984
C	0.2050	12.7588	1.2696	**C**	5.1702	-4.4796	0.0001	**H**	-7.6916	-1.0818	-2.1698
C	0.2051	12.7587	-1.2699	**C**	3.9923	-3.7383	0.0001	**H**	-3.4351	-5.9170	-1.2992
C	0.0956	7.4697	0.0000	**C**	3.9927	-2.3473	0.0001	**H**	-4.3465	-7.4309	-1.3007
C	1.2944	6.7172	0.0001	**C**	5.2262	-1.7013	0.0000	**H**	-4.9750	-6.0207	-2.1706
C	1.2413	5.3265	0.0001	**C**	6.4278	-2.4005	0.0000	**H**	7.5240	-9.8945	0.0000
C	0.0364	4.6314	0.0001	**C**	7.6977	-1.5681	-0.0001	**H**	5.4222	-8.5912	0.0000

C	-1.1397	5.3767	0.0000	**C**	7.7135	-0.6762	1.2694	**H**	9.6761	-8.6778	0.0000
C	-1.1350	6.7669	-0.0001	**C**	5.0204	-5.9903	0.0001	**H**	10.1885	-0.7186	-0.0001
C	-2.4908	7.4504	-0.0001	**C**	4.2371	-6.4174	1.2694	**H**	12.3175	-1.9768	-0.0001
C	-3.2711	7.0182	1.2693	**C**	4.2370	-6.4173	-1.2692	**H**	12.2370	-4.4477	-0.0001
C	2.6776	7.3428	0.0001	**C**	7.7134	-0.6763	-1.2695	**H**	10.4147	-6.2346	2.1700
C	3.4390	6.8781	1.2694	**H**	4.8069	11.4631	0.0001	**H**	11.0407	-7.6461	1.3007
C	3.4391	6.8780	-1.2692	**H**	4.7291	8.9912	0.0001	**H**	11.9556	-6.1348	1.3007
C	-3.2710	7.0182	-1.2696	**H**	2.6772	12.7186	-0.0001	**H**	11.9556	-6.1349	-1.3008
C	-11.4019	-2.1303	0.0003	**H**	-4.4719	9.1828	-0.0003	**H**	11.0407	-7.6462	-1.3007
C	-10.1768	-1.4840	0.0004	**H**	-4.4467	11.6557	-0.0003	**H**	10.4147	-6.2346	-2.1701
C	-8.9681	-2.1839	0.0003	**H**	-2.2666	12.8214	-0.0003	**H**	3.0367	-4.2472	0.0002
C	-8.9768	-3.5968	0.0001	**H**	0.1920	12.1367	2.1699	**H**	5.2379	-0.6184	0.0001
C	-10.2234	-4.2610	0.0001	**H**	1.1015	13.3846	1.3006	**H**	7.7018	-1.2978	2.1701
C	-11.4049	-3.5151	0.0002	**H**	-0.6648	13.4213	1.3005	**H**	8.6087	-0.0485	1.3001
N	-7.7564	-4.3345	0.0000	**H**	1.1016	13.3845	-1.3009	**H**	6.8419	-0.0161	1.2988
C	-7.7871	-5.7600	-0.0002	**H**	0.1922	12.1365	-2.1702	**H**	4.7829	-6.1200	2.1702
C	-9.0157	-6.4570	-0.0002	**H**	-0.6647	13.4212	-1.3010	**H**	3.2488	-5.9497	1.2989
C	-10.3703	-5.7719	-0.0001	**H**	2.1598	4.7534	0.0002	**H**	4.0944	-7.5014	1.2996
C	-6.5893	-6.5095	-0.0003	**H**	-2.0834	4.8453	0.0000	**H**	4.0944	-7.5014	-1.2995
C	-6.6456	-7.9051	-0.0005	**H**	-2.7271	7.3189	2.1700	**H**	3.2488	-5.9497	-1.2987
C	-7.8476	-8.5936	-0.0005	**H**	-4.2624	7.4796	1.2999	**H**	4.7828	-6.1200	-2.1701
C	-9.0186	-7.8543	-0.0004	**H**	-3.4070	5.9334	1.2987	**H**	6.8419	-0.0162	-1.2989
C	-11.1519	-6.2019	1.2697	**H**	2.9086	7.2021	2.1703	**H**	8.6086	-0.0486	-1.3003
C	-11.1520	-6.2017	-1.2698	**H**	3.5282	5.7884	1.2990	**H**	7.7017	-1.2979	-2.1703

Table S4. Cartesian coordinates [Å] of the optimized structure for **TTT-3tBu**.

	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 S5. Cartesian coordinates [Å] of the optimized structure for **TTTD-3tBu**.

	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
N	-1.2301	-0.5671	0.0061	C	-5.2079	7.7274	1.9163	H	-10.0446	-9.2630	-3.4381
C	-0.1239	-1.3943	0.0052	C	-5.9381	9.0391	0.0344	H	-11.0263	-5.4876	-1.5393
N	1.1045	-0.7781	0.0069	C	-7.1513	9.2627	0.6731	H	-12.3169	-6.5472	-2.1443
C	1.2678	0.5936	0.0084	C	-7.4379	8.7194	1.9365	H	-11.3924	-7.0050	-0.7053
N	0.1199	1.3493	0.0090	C	-6.4377	7.9446	2.5360	H	-1.4592	-12.8707	3.3819
C	-1.1496	0.8049	0.0073	C	-8.7972	8.9870	2.5944	H	-1.5676	-11.1062	3.4805
N	0.0195	2.7141	0.0091	C	-8.9213	8.3127	3.9704	H	-1.2759	-11.8829	1.9174
C	-1.3009	2.8990	0.0091	C	-1.1062	12.5090	-2.6272	H	-5.1578	-12.2814	3.8135
N	-2.0600	1.7393	0.0076	C	-1.1533	13.8126	-1.8136	H	-3.7397	-13.1040	4.4964
N	2.3367	-1.3735	0.0060	C	-8.9837	10.5083	2.7833	H	-3.8879	-11.3437	4.6136
C	3.1570	-0.3225	0.0084	C	-9.9210	8.4420	1.6862	H	-2.3902	12.4343	-0.1350
N	2.5322	0.9148	0.0096	C	0.3745	12.1482	-2.8763	H	-3.4640	10.5294	0.9681
N	-2.3619	-1.3364	0.0033	C	-1.8075	12.7584	-3.9803	H	-2.5024	8.0321	-2.3836
C	-1.8618	-2.5724	0.0025	C	10.7223	-4.1130	-1.9076	H	-1.4003	9.9261	-3.4815
N	-0.4779	-2.6499	0.0032	C	11.1380	-3.6586	-0.6503	H	-4.4468	7.1329	2.4111
C	-1.9106	4.2229	0.0106	C	10.5094	-2.5905	-0.0119	H	-5.7477	9.4637	-0.9458
C	-3.3067	4.3589	-0.0101	C	9.4452	-1.9247	-0.6265	H	-7.8973	9.8663	0.1644
C	-3.8963	5.6145	-0.0157	C	9.0235	-2.3567	-1.8916	H	-6.6001	7.5063	3.5139
C	-3.1038	6.7760	0.0113	C	9.6474	-3.4349	-2.5064	H	-9.9052	8.5301	4.3999
C	-1.7029	6.6384	0.0391	N	8.8173	-0.8222	0.0115	H	-8.8235	7.2239	3.8987

C	-1.1184	5.3820	0.0329	C	9.6278	0.1498	0.6565	H	-8.1642	8.6803	4.6718
C	-2.7034	-3.7624	0.0011	C	9.2908	0.6433	1.9202	H	-0.6491	14.6115	-2.3681
C	4.6084	-0.4563	0.0101	C	10.7931	0.6237	0.0391	H	-2.1829	14.1370	-1.6265
C	-4.1036	-3.6558	0.0223	C	11.5929	1.5613	0.6802	H	-0.6455	13.7067	-0.8486
C	-4.8994	-4.7900	0.0259	C	11.2649	2.0786	1.9444	H	-9.9540	10.7194	3.2484
C	-4.3182	-6.0722	-0.0033	C	10.0934	1.5985	2.5423	H	-8.9467	11.0425	1.8285
C	-2.9161	-6.1777	-0.0300	C	12.1757	3.1208	2.6049	H	-8.1984	10.9189	3.4275
C	-2.1234	-5.0392	-0.0216	C	11.6532	3.5622	3.9817	H	-9.8124	7.3617	1.5396
C	5.4242	0.6847	-0.0080	C	11.3833	-5.2913	-2.6333	H	-10.9023	8.6298	2.1382
C	6.8064	0.5676	-0.0133	C	12.5356	-5.9036	-1.8203	H	-9.9106	8.9164	0.6997
C	7.4161	-0.6995	0.0115	C	13.5866	2.5217	2.7930	H	0.8844	12.9666	-3.3986
C	6.5965	-1.8440	0.0367	C	12.2655	4.3686	1.6995	H	0.4741	11.2466	-3.4890
C	5.2161	-1.7220	0.0301	C	10.3306	-6.3928	-2.8845	H	0.8953	11.9689	-1.9294
C	-3.8214	-10.8070	1.8948	C	11.9504	-4.8065	-3.9854	H	-2.8606	13.0201	-3.8296
C	-4.4374	-10.8274	0.6379	H	-3.9221	3.4662	-0.0365	H	-1.3222	13.5833	-4.5156
C	-4.8540	-9.6564	0.0063	H	-4.9760	5.7068	-0.0446	H	-1.7711	11.8742	-4.6245
C	-4.6817	-8.4165	0.6278	H	-1.0813	7.5260	0.0707	H	11.9598	-4.1462	-0.1389
C	-4.0788	-8.3771	1.8927	H	-0.0381	5.2852	0.0609	H	10.8465	-2.2657	0.9670
C	-3.6516	-9.5508	2.5006	H	-4.5598	-2.6718	0.0515	H	8.2043	-1.8440	-2.3851
N	-5.1256	-7.2238	-0.0028	H	-5.9790	-4.6956	0.0560	H	9.2940	-3.7436	-3.4858
C	-6.3906	-7.2195	-0.6488	H	-2.4561	-7.1588	-0.0613	H	8.3951	0.2804	2.4137
C	-6.5527	-6.6391	-1.9100	H	-1.0426	-5.1260	-0.0476	H	11.0662	0.2484	-0.9417
C	-7.5020	-7.8122	-0.0343	H	4.9588	1.6641	-0.0327	H	12.4888	1.9067	0.1727
C	-8.7341	-7.8215	-0.6758	H	7.4261	1.4566	-0.0402	H	9.7944	1.9563	3.5207
C	-8.9201	-7.2324	-1.9375	H	7.0544	-2.8262	0.0665	H	12.3331	4.3048	4.4131
C	-7.8002	-6.6393	-2.5325	H	4.5922	-2.6093	0.0560	H	10.6613	4.0217	3.9107
C	-10.3037	-7.2598	-2.5985	H	-4.5909	-11.7677	0.1213	H	11.5931	2.7212	4.6813
C	-10.3069	-6.5694	-3.9722	H	-5.3201	-9.7012	-0.9725	H	12.9754	-6.7388	-2.3760
C	-3.3410	-12.0740	2.6131	H	-3.9458	-7.4225	2.3911	H	13.3313	-5.1745	-1.6319
C	-3.6110	-13.3462	1.7934	H	-3.1873	-9.4832	3.4801	H	12.1897	-6.2919	-0.8560
C	-10.7489	-8.7256	-2.7935	H	-5.6995	-6.1831	-2.4015	H	14.2542	3.2557	3.2598
C	-11.3189	-6.5325	-1.6900	H	-7.3896	-8.2667	0.9446	H	14.0311	2.2248	1.8377
C	-1.8204	-11.9744	2.8637	H	-9.5739	-8.2895	-0.1707	H	13.5496	1.6349	3.4353
C	-4.0755	-12.2054	3.9652	H	-7.8825	-6.1762	-3.5089	H	11.2756	4.8146	1.5536
C	-1.7973	11.3470	-1.9033	H	-11.3126	-6.6129	-4.4041	H	12.9184	5.1237	2.1535
C	-2.4007	11.4791	-0.6469	H	-10.0234	-5.5139	-3.8962	H	12.6716	4.1247	0.7126
C	-3.0125	10.4004	-0.0101	H	-9.6228	-7.0594	-4.6738	H	10.7846	-7.2427	-3.4080
C	-3.0560	9.1462	-0.6254	H	-3.2523	-14.2225	2.3441	H	9.5002	-6.0273	-3.4968
C	-2.4689	8.9976	-1.8896	H	-4.6810	-13.4877	1.6047	H	9.9146	-6.7557	-1.9382
C	-1.8460	10.0774	-2.5028	H	-3.0919	-13.3248	0.8289	H	12.7036	-4.0256	-3.8333
N	-3.6980	8.0509	0.0109	H	-11.7401	-8.7648	-3.2609	H	12.4223	-5.6383	-4.5220
C	-4.9464	8.2665	0.6535	H	-10.8065	-9.2614	-1.8407	H	11.1666	-4.3948	-4.6292

Table S6. Cartesian coordinates [Å] of the optimized structure for **TTT-3ACR**.

	X	Y	Z		X	Y	Z		X	Y	Z
N	1.3082	-0.4273	0.1211	C	9.2602	3.1002	-2.8936	H	6.8651	-1.7244	-1.2653
C	0.2910	-1.3712	0.0785	C	10.1557	2.5495	-1.9815	H	3.6082	0.9821	1.3214
N	-1.0240	-0.9189	0.1211	C	11.9052	0.3359	-0.8559	H	4.4491	-2.3633	-1.2492
C	-1.3328	0.4340	0.0786	C	11.4491	2.2398	0.7483	H	11.1790	-1.8827	3.5804
N	-0.2836	1.3466	0.1211	C	-4.0166	9.8212	2.8499	H	8.7385	-2.4416	3.5540
C	1.0424	0.9376	0.0786	C	-3.0685	8.8000	2.8335	H	7.2624	-1.4013	1.8926
C	-0.2033	2.7445	0.0322	C	-3.1581	7.7804	1.8943	H	12.0645	-0.2853	1.9298
N	1.0658	3.0842	-0.0445	C	-4.2000	7.7616	0.9479	H	6.4535	1.5228	-1.8353
N	1.8531	1.9496	-0.0207	C	-5.1671	8.7847	0.9538	H	7.1968	3.1332	-3.5298
C	-2.2748	-1.5483	0.0321	C	-5.0463	9.7957	1.9138	H	9.6046	3.8120	-3.6374
N	-3.2035	-0.6190	-0.0446	N	-4.2687	6.7204	0.0075	H	11.1994	2.8449	-2.0307
N	-2.6145	0.6301	-0.0207	C	-5.2925	6.6513	-0.9528	H	11.4697	-0.4957	-1.4184

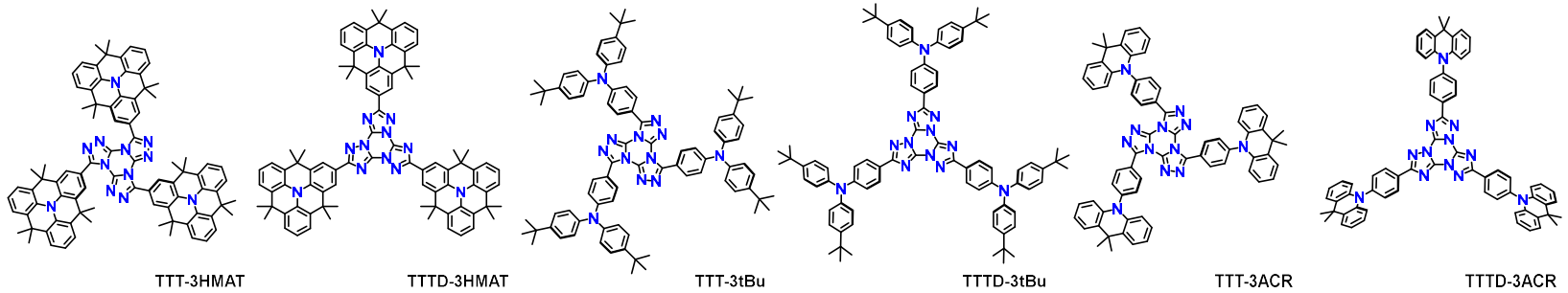
C	2.4786	-1.1959	0.0321	C	-6.2934	7.6399	-1.0026	H	12.3850	1.0152	-1.5674
N	2.1382	-2.4647	-0.0447	C	-6.3306	8.8276	-0.0389	H	12.6834	-0.0663	-0.1996
N	0.7619	-2.5793	-0.0208	C	-5.3156	5.5866	-1.8731	H	11.9189	2.9591	0.0703
C	-2.0787	5.8902	-0.7028	C	-6.3176	5.4967	-2.8311	H	10.6879	2.7672	1.3314
C	-3.2611	5.7077	0.0191	C	-7.3162	6.4669	-2.8922	H	12.2181	1.8782	1.4380
C	-3.4574	4.5350	0.7501	C	-7.2869	7.5182	-1.9806	H	-3.9583	10.6243	3.5780
C	-1.1019	4.9022	-0.6984	C	-6.2452	10.1409	-0.8567	H	-2.2536	8.7906	3.5518
C	-1.3017	3.7135	0.0249	C	-7.6644	8.7941	0.7489	H	-2.4168	6.9912	1.8915
C	-2.4843	3.5405	0.7576	C	-6.4972	-8.3876	2.8506	H	-5.7852	10.5911	1.9284
C	-2.1986	-5.2616	0.7500	C	-6.0863	-7.0560	2.8341	H	-4.5457	4.8263	-1.8346
C	-3.3123	-5.6780	0.0189	C	-5.1585	-6.6243	1.8946	H	-6.3127	4.6635	-3.5281
C	-4.0614	-4.7452	-0.7032	C	-4.6219	-7.5175	0.9482	H	-8.1052	6.4087	-3.6356
C	-1.8237	-3.9217	0.7574	C	-5.0249	-8.8664	0.9542	H	-8.0649	8.2741	-2.0297
C	-2.5647	-2.9840	0.0246	C	-5.9608	-9.2668	1.9144	H	-5.3076	10.1797	-1.4198
C	-3.6940	-3.4053	-0.6987	N	-3.6858	-7.0568	0.0075	H	-7.0738	10.2162	-1.5677
C	5.6564	0.7269	0.7499	C	-3.1145	-7.9092	-0.9527	H	-6.2859	11.0162	-0.2007
C	6.5739	-0.0295	0.0191	C	-3.4707	-9.2701	-1.0024	H	-8.5228	8.8407	0.0715
C	6.1406	-1.1449	-0.7028	C	-4.4811	-9.8957	-0.0386	H	-7.7398	7.8715	1.3326
C	4.3085	0.3816	0.7574	C	-2.1807	-7.3973	-1.8731	H	-7.7357	9.6412	1.4384
C	3.8671	-0.7291	0.0247	C	-1.6022	-8.2204	-2.8310	H	-7.2218	-8.7384	3.5790
C	4.7965	-1.4966	-0.6984	C	-1.9438	-9.5702	-2.8921	H	-6.4852	-6.3454	3.5525
C	10.5129	-1.4310	2.8518	C	-2.8690	-10.0700	-1.9804	H	-4.8453	-5.5879	1.8917
C	9.1544	-1.7412	2.8353	C	-5.6616	-10.4775	-0.8564	H	-6.2806	-10.3043	1.9291
C	8.3165	-1.1542	1.8954	C	-3.7858	-11.0346	0.7490	H	-1.9068	-6.3505	-1.8346
C	8.8217	-0.2432	0.9486	H	-1.9392	6.8074	-1.2655	H	-0.8830	-7.8000	-3.5281
C	10.1914	0.0824	0.9545	H	-4.3776	4.4103	1.3109	H	-1.4992	-10.2246	-3.6354
C	11.0061	-0.5273	1.9152	H	-0.1777	5.0346	-1.2493	H	-3.1352	-11.1215	-2.0295
N	7.9547	0.3364	0.0075	H	-2.6541	2.6337	1.3217	H	-6.1635	-9.6845	-1.4194
C	8.4072	1.2569	-0.9532	H	-1.6306	-5.9962	1.3108	H	-5.3129	-11.2329	-1.5676
C	9.7639	1.6290	-1.0030	H	-4.9254	-5.0828	-1.2658	H	-6.3994	-10.9501	-0.2004
C	10.8108	1.0676	-0.0388	H	-0.9536	-3.6154	1.3216	H	-4.4840	-11.5195	1.4384
C	7.4970	1.8090	-1.8740	H	-4.2707	-2.6711	-1.2497	H	-3.3975	-11.8014	0.0714
C	7.9206	2.7210	-2.8324	H	6.0085	1.5862	1.3106	H	-2.9488	-10.6392	1.3326

Table S7. Cartesian coordinates [Å] of the optimized structure for **TTTD-3ACR**.

	X	Y	Z		X	Y	Z		X	Y	Z
N	0.1762	-1.3422	0.0001	C	6.5635	-8.6432	-3.7117	H	0.8550	7.5338	0.0007
C	1.2958	-0.5336	-0.0001	C	6.9986	-9.2124	-2.5185	H	4.8110	5.8968	-0.0008
N	1.0740	0.8237	-0.0002	C	6.6816	-10.8791	-0.0002	H	3.8627	3.5844	-0.0009
C	-0.1861	1.3890	-0.0001	C	8.6917	-9.3411	0.0002	H	6.8786	-9.0591	4.6638
N	-1.2507	0.5183	0.0000	C	4.2040	10.0057	-3.7117	H	5.3608	-7.0698	4.5725
C	-1.1102	-0.8556	0.0001	C	3.6671	8.7207	-3.6589	H	4.6673	-6.1578	2.4022
N	-2.5809	0.8294	0.0000	C	3.4155	8.1199	-2.4319	H	7.6562	-10.0754	2.5608
C	-3.1509	-0.3739	0.0000	C	3.6966	8.7935	-1.2282	H	4.6675	-6.1576	-2.4021
N	-2.2739	-1.4445	0.0001	C	4.2393	10.0921	-1.2654	H	5.3615	-7.0692	-4.5724
N	2.0086	1.8201	-0.0002	C	4.4798	10.6669	-2.5184	H	6.8797	-9.0582	-4.6638
C	1.2514	2.9154	-0.0001	N	3.4330	8.1648	0.0000	H	7.6570	-10.0748	-2.5608
N	-0.1142	2.6912	0.0000	C	3.6968	8.7933	1.2282	H	5.5888	-10.9377	-0.0003
N	0.5718	-2.6498	0.0002	C	4.2395	10.0919	1.2655	H	7.0520	-11.4068	-0.8847
C	1.8989	-2.5417	0.0000	C	4.5703	10.8857	0.0001	H	7.0518	-11.4070	0.8842
N	2.3876	-1.2469	-0.0002	C	3.4160	8.1194	2.4318	H	9.1044	-9.8364	-0.8843
C	-4.6024	-0.5571	0.0000	C	3.6679	8.7200	3.6589	H	9.0341	-8.3016	0.0003
C	-5.1405	-1.8516	0.0003	C	4.2048	10.0050	3.7118	H	9.1042	-9.8365	0.8847
C	-6.5203	-2.0311	0.0003	C	4.4803	10.6664	2.5186	H	4.4054	10.4870	-4.6637
C	-7.3705	-0.9232	0.0000	C	3.7462	12.1979	0.0003	H	3.4408	8.1782	-4.5725
C	-6.8366	0.3692	-0.0002	C	6.0824	11.2240	0.0000	H	2.9980	7.1214	-2.4022

C	-5.4592	0.5544	-0.0002	C	-10.7672	-1.3623	-3.7118	H	4.8980	11.6680	-2.5607
C	2.7834	-3.7072	0.0000	C	-9.3860	-1.1846	-3.6589	H	2.9985	7.1209	2.4021
C	1.8186	4.2641	-0.0001	C	-8.7399	-1.1021	-2.4318	H	3.4417	8.1774	4.5724
C	2.2492	-5.0049	0.0004	C	-9.4639	-1.1957	-1.2282	H	4.4064	10.4861	4.6639
C	3.0983	-6.1052	0.0004	C	-10.8599	-1.3750	-1.2655	H	4.8986	11.6675	2.5609
C	4.4845	-5.9214	0.0001	C	-11.4778	-1.4541	-2.5185	H	2.6747	11.9756	0.0004
C	5.0188	-4.6311	-0.0003	N	-8.7877	-1.1096	0.0000	H	3.9696	12.8026	0.8848
C	4.1734	-3.5259	-0.0003	C	-9.4640	-1.1952	1.2282	H	3.9694	12.8027	-0.8842
C	0.9666	5.3773	0.0003	C	-10.8600	-1.3745	1.2655	H	6.3549	11.8083	0.8844
C	1.5011	6.6621	0.0003	C	-11.7127	-1.4853	0.0000	H	6.6788	10.3065	-0.0001
C	2.8857	6.8443	-0.0001	C	-8.7401	-1.1013	2.4318	H	6.3548	11.8084	-0.8845
C	3.7379	5.7357	-0.0005	C	-9.3862	-1.1834	3.6589	H	-11.2847	-1.4285	-4.6638
C	3.2096	4.4503	-0.0005	C	-10.7675	-1.3609	3.7117	H	-8.8030	-1.1093	-4.5725
C	6.5627	-8.6439	3.7118	C	-11.4780	-1.4532	2.5185	H	-7.6665	-0.9644	-2.4021
C	5.7179	-7.5367	3.6589	C	-12.4366	-2.8553	0.0002	H	-12.5539	-1.5926	-2.5608
C	5.3236	-7.0184	2.4319	C	-12.7621	-0.3453	-0.0003	H	-7.6666	-0.9636	2.4022
C	5.7671	-7.5982	1.2282	H	-4.4694	-2.7032	0.0005	H	-8.8033	-1.1078	4.5725
C	6.6208	-8.7172	1.2655	H	-6.9522	-3.0265	0.0004	H	-11.2851	-1.4268	4.6637
C	6.9980	-9.2130	2.5185	H	-7.5127	1.2179	-0.0004	H	-12.5541	-1.5916	2.5607
N	5.3545	-7.0555	0.0000	H	-5.0359	1.5530	-0.0004	H	-11.7081	-3.6719	0.0004
C	5.7673	-7.5980	-1.2282	H	1.1727	-5.1377	0.0006	H	-13.0720	-2.9643	0.8847
C	6.6211	-8.7169	-1.2655	H	2.7013	-7.1150	0.0006	H	-13.0720	-2.9646	-0.8843
C	7.1434	-9.4000	0.0000	H	6.0969	-4.5074	-0.0005	H	-13.4044	-0.4016	0.8841
C	5.3239	-7.0180	-2.4318	H	4.5754	-2.5189	-0.0005	H	-12.2660	0.6302	-0.0004
C	5.7185	-7.5362	-3.6588	H	-0.1065	5.2220	0.0006	H	-13.4043	-0.4019	-0.8848

Comparison of TTT and TTTD Properties



Scheme S2. TTT-based compounds (**TTT-3HMAT**,[2] **TTT-3tBu**,[2] **TTT-3ACR**[6]) reported previously, in addition to the Dimroth-rearranged product discussed in this work.

Table S8. Comparison of photophysical and electrochemical for TTT and TTTD compounds.

	Photophysical – In Toluene							Electrochemical (CV)	Photophysical – In Doped Films [e]				
	λ_{abs} (nm) ε (10^4 cm^{-1} M^{-1})	λ_{em} (nm)	CIE (x,y)	Φ_{air}/Φ_{N2}	$\sigma^2_{740\ nm}$ (GM)	τ_{air}	τ_{N2}	HOMO/LUMO (eV)	λ_{em} (nm)	CIE (x,y)	Φ_{air}	τ_{air}	τ_{N2}
TTT-3HMAT [2] [a]	296 (5.7) 383 (7.4)	430	(0.15, 0.06)	0.94/0.95	2930	2.1 ns	2.5 ns	–5.30/–2.27 [b]	434	(0.16, 0.07)	0.77	2.6 ns	2.6 ns
TTTD-3HMAT	298 (11) 391 (11)	416	(0.16, 0.03)	1.00/1.00	1001	2.1 ns	2.3 ns	–4.97/–1.91 [c]	425	(0.16, 0.05)	1.00	2.7 ns	2.7 ns
TTT-3tBu [2] [a]	296 (3.8) 362 (6.4)	440	(0.15, 0.08)	0.86/0.89	350	2.8 ns	3.2 ns	–5.30/–2.13 [b]	440	(0.16, 0.09)	0.77	3.2 ns	3.2 ns
TTTD-3tBu	298 (4.1) 370 (10)	428	(0.16, 0.05)	1.00/1.00	845	2.6 ns	2.6 ns	–5.01/–1.85 [c]	432	(0.15, 0.06)	1.00	3.5 ns	3.5 ns
TTT-3ACR [6] [a]	284 (-) 361 (-)	477	(0.16, 0.23)	-	-	-	-	–5.04/–3.46 [d]	464	(0.17, 0.19)	0.41	11.7 ns / 143 µs	-
TTTD-3ACR	363 (0.5)	461	(0.15, 0.16)	0.26/0.41	83	7.6 ns	11 ns / 19 µs	–4.98/–1.92 [c]	454	(0.16, 0.15)	0.14	9.2 ns / 107 µs	9.2 ns / 13 ms

[a] Values taken from literature. [b] CV performed in *N,N*-dimethylformamide against $Fc^{0/+}$, where LUMO = (E_{gap}^{opt} + HOMO), and HOMO = –($E_{1/2,ox}$ + 4.8 eV). [c] CV performed in *o*-difluorobenzene against $Fc^{0/+}$, where LUMO = (E_{gap}^{opt} + HOMO), and HOMO = –($E_{1/2,ox}$ + 4.8 eV). [d] CV performed in acetonitrile against $Fc^{0/+}$, where LUMO = –($E_{1/2,red}$ + 4.8 eV), and HOMO = –($E_{1/2,ox}$ + 4.8 eV). [e] 3 to 4 wt%-doped PMMA used for all films, except for **TTT-3ACR** where 3 wt%-doped DPEPO or PMMA was used.

Thermal Characterization

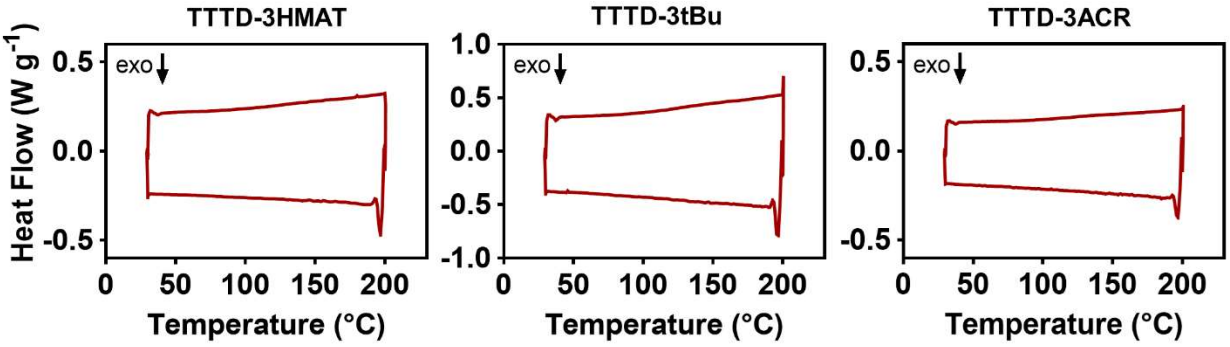


Figure S16. Differential scanning calorimetry (DSC) traces, run over a temperature range of 30 to 200 °C for two heating and cooling cycles at 10 °C min^{-1}, with the second cycle shown in each case.

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