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Boosting emission efficiency and suppressing device-efficiency roll-off for TADF emitters by modulating molecular conformation and intra-/intermolecular interactions

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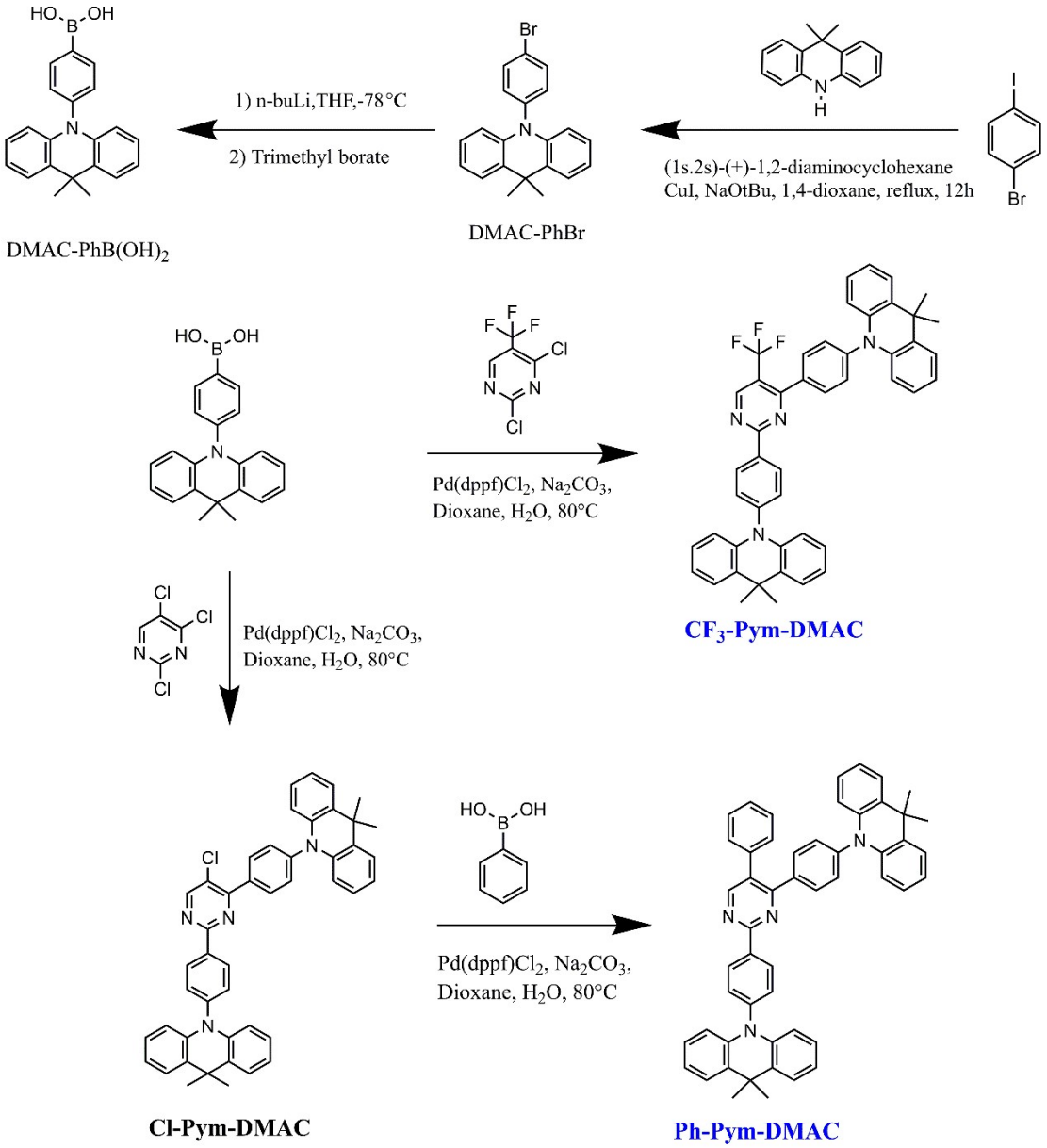
Content

1. General Methods

All reactions were taken under an N_2 atmosphere using standard Schlenk techniques. All reagents and solvents were obtained commercially and used without further purification. Dry tetrahydrofuran, dry toluene, dry 1,4-dioxane and dry dichloromethane (DCM) were purchased from Adamas Reagent, Ltd. All compounds were purified by column chromatography and dried, the prepared TADF material is further purified by sublimation before device fabrication. Single crystal X-ray diffraction data were collected at 200 K on a Bruker–D8 VENTRUE diffractometer with X-ray source of Mo Kα. NMR (500 MHz) spectra were recorded on a Bruker Avance III NMR spectrometer, in deuterated chloroform ($CDCl_3$). Thermogravimetric analyses (TGA) were performed on a METTLER TOLEDO system with a heating rate of 10 °C/min under nitrogen. UV-Vis absorption spectra were recorded with a Agilent Cary 5000 UV-Vis spectrophotometer under ambient condition. The absolute PLQYs were measured on an Edinburgh FLS1000 spectrophotometer equipped with an integrating sphere. Steady-state PL spectra were measured on an Edinburgh FLS980 using a Xenon lamp as an excitation light source. The transient PL decay curves were measured on the same spectrophotometer (FLS980) in time-correlated single-photon counting (TCSPC) mode with a NT242-1K OPO laser as an excitation light source. The time-resolved PL spectra were recorded on an Edinburgh LP980 spectrophotometer with a NT242-1K OPO laser excitation source.

2. Material Synthesis and Characterization



Scheme S1. Synthetic route of CF_3-Pym-DMAC and Ph-Pym-DMAC.

1.1 Synthesis of DMAC-PhBr

The synthesis process of DMAC-PhBr was referred to the reported literature.[1]

1.2 Synthesis of DMAC-PhB(OH)$_2$

The synthesis process was referred to the reported literature.[2]

1.3 Synthesis of CF_3-Pym-DMAC

DMAC-PhB(OH)$_2$ (1.78 g, 5.4 mmol), 2,4-Dichloro-5-(trifluoromethyl)pyrimidine (542 mg, 2.5 mmol), Pd(dppf)Cl_2 (220 mg, 0.27 mmol) and base Na_2CO_3 (1.14 g, 10.8

mmol) were suspended in 1,4-dioxane/water (28 : 4 mL). The mixture was stirred at 80 ℃ under an argon atmosphere for or a period time (usually 2-6 h) until the completion of the reaction as monitored by TLC. The cooled mixture was diluted with water and exhaustively extracted with ethyl acetate (30 mL, three times). The organic phase was washed by brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The deposit was purified by silica-gel column chromatography using ethyl acetate/petroleum ether (10:1) as the eluent to obtain the products. Yellowish green solid, yield: 94%.^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.87 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.3 Hz, 2H), 7.61 – 7.36 (m, 8H), 7.09 – 6.73 (m, 8H), 6.37 (ddd, J = 7.8, 3.4, 1.3 Hz, 4H), 1.72 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.85 (s), 165.17 (s), 156.41 (s), 144.98 (s), 143.41 (s), 140.58 (d, J = 9.1 Hz), 136.79 (s), 135.85 (s), 131.85 – 131.38 (m), 131.27 (s), 130.34 (s), 126.42 (d, J = 6.3 Hz), 125.30 (d, J = 8.6 Hz), 120.90 (d, J = 3.9 Hz), 114.18 (d, J = 3.2 Hz), 77.26 (s), 77.01 (s), 76.75 (s), 36.04 (s), 31.17 (d, J = 15.9 Hz). Anal. Calcd for $C_{47}H_{37}N_4F_3$: C, 78.97; H, 5.22; N, 7.84. Found: C, 78.56; H, 5.28; N, 7.69. ESI-APCI: m/z calcd. for $C_{47}H_{37}N_4F_3$ $[M + H]^+$, 715.3043; found, 715.3050.

1.4 Synthesis of Cl-Pym-DMAC

Synthesis processes for Cl-Pym-DMAC are the same as CF_3-Pym-DMAC but replacement of the reactive material. Yellowish green solid, yield: 40%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.86 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 7.6 Hz, 4H), 7.50 – 7.47 (m, 4H), 7.00 (m, J = 8H), 6.39 – 6.35 (m, 4H), 1.71 (s, 12H).

1.5 Synthesis of Ph-Pym-DMAC

Synthesis processes for Ph-Pym-DMAC was similar to CF_3-Pym-DMAC but replacement of the reactive material. Yellow-white solid, yield: 72%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.88 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.51 – 7.35 (m, 9H), 7.32 (d, J = 8.5 Hz, 2H), 7.04 – 6.89 (m, 8H), 6.42 (dd, J = 8.0, 1.2 Hz, 2H), 6.32 (dd, J = 8.1, 1.2 Hz, 2H), 1.70 (d, J = 20.0 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.64 (d, J = 13.1 Hz), 132.53 (s), 131.36 (d, J = 19.9 Hz), 131.01 (d, J = 10.9 Hz), 130.24 (s), 129.38 (s), 128.91 (s), 128.40 (s), 126.36 (d, J = 8.4 Hz), 125.26 (d, J = 4.5 Hz), 120.76 (d, J = 5.2 Hz), 114.17 (d, J = 18.2 Hz), 77.26 (s), 77.01

(s), 76.75 (s), 36.02 (d, J = 5.0 Hz), 31.27 (s), 31.11 (s). Anal. Calcd for $C_{52}H_{42}N_4$: C, 86.39; H, 5.86; N, 7.75. Found: C, 86.54; H, 5.66; N, 7.82. ESI-APCI: m/z calcd. for $C_{52}H_{42}N_4$ $[M + H]^+$, 722.3482; found, 723.3502.

3. Theoretical Calculations

All calculations are performed using the Gaussian 09 package. The ground state geometry of the studied compounds is calculated by functional theory of PEB0/6-311G (d, p). Using the optimized ground state geometry, the front-line molecular orbital and excited state molecular configuration of the molecule were obtained by the calculation of time-density functional theory (TD-DFT). The spin-orbit couplings were calculated at PBE0/DKH by ORCA. Use the GaussView program to generate visualized geometrically optimized structures and front-line molecular orbitals, and Multiwfn 2.4 to aid in the analysis of molecular orbital components.

Table S1. Calculated energy levels of the excited states and the FMOs.

	S_1 [eV]	T_1 [eV]	T_2 [eV]	T_3 [eV]	T_4 [eV]	ΔE_{ST} [eV]	HOMO [eV]	LUMO [eV]
Ph-Pym-DMAC	2.710	2.700	2.793	2.843	3.076	0.010	-5.28	-1.98
CF_3-Pym-DMAC	2.455	2.446	2.708	2.938	2.947	0.009	-5.25	-2.32

Table S2. Calculated energy levels spin-orbit couplings.

	SOC_{S1-T1} [cm^{-1}]	SOC_{S1-T2} [cm^{-1}]	SOC_{S1-T3} [cm^{-1}]	SOC_{S1-T4} [cm^{-1}]
Ph-Pym-DMAC	0.48	0.044	0.014	0.15
CF_3-Pym-DMAC	0.30	0.044	0.600	0.82

Table S3. Local excitation (LE) characters (in %) for the S_1 and T_{1-4} states.

	S_1 LE(%)	T_1 LE(%)	T_2 LE(%)	T_3 LE(%)	T_4 LE(%)
Ph-Pym-DMAC	9.90	10.2	10.1	99.6	18.1
CF_3-Pym-DMAC	9.67	9.89	9.36	9.37	99.1

Table S4. The lowest excited singlet (S_1) and triplet (T_{1-4}) energies,and transition configurations of Ph-Pym-DMAC and CF_3-Pym-DMAC calculated by TD-DFT at the PEB0/6-311G (d, p).

compound	state	E (eV)	Main configuration
Ph-Pym-DMAC	S_1	2.710	H→L 0.845 H→L+1 0.128
	T_1	2.700	H→L 0.838 H→L+1 0.132
	T_2	2.793	H-1→L 0.864 H-1→L+1 0.106
	T_3	2.843	H-2→L 0.630 H-2→L+1 0.064
	T_4	3.076	H→L+1 0.742 H→L 0.121
CF_3-Pym-DMAC	S_1	2.455	H→L 0.921 H→L+1 0.060
	T_1	2.446	H→L 0.917 H→L+1 0.063
	T_2	2.708	H-1→L 0.881 H-1→L+1 0.094
	T_3	2.938	H→L+1 0.889 H→L 0.063
	T_4	2.947	H-8→L 0.645 H-8→L+1 0.081

H → L represents the HOMO to LUMO transition. Excitation configurations with the highest contributions are presented, together with the corresponding transition symmetry and nature of the involved orbitals.

Table S5. Calculated XYZ coordinates of CF_3-Pym-DMAC at optimized S_0 state.

Atomic Type	Coordinates (Angstroms)			Atomic Type	Coordinates (Angstroms)		
	X	Y	X		X	Y	Z
F	-3.23655	4.332037	0.387347	C	-6.83124	0.762567	1.205919
F	-2.9337	4.719113	-1.7174	C	-6.72722	-0.56102	0.767644
F	-2.02282	5.994849	-0.24534	C	-6.77276	-3.52649	1.850951
N	-5.56798	-1.02493	0.122504	C	-1.09828	3.856933	-0.49599
N	0.081474	1.82148	-0.22571	C	0.142015	4.478651	-0.60878
N	6.107613	-0.35637	0.116663	C	-2.32836	4.716617	-0.51358
N	1.292393	3.830617	-0.54993	C	3.704584	2.442535	-0.27641
C	-8.88498	-3.69875	0.545155	C	4.896247	1.744049	-0.16517

C	-7.5737	-2.92746	0.672123	H	-9.50133	-3.32119	-0.27544
C	-6.71238	-3.04081	-0.57667	H	-9.46042	-3.63501	1.471388
C	-5.66208	-2.12258	-0.74951	H	-8.69225	-4.76061	0.376556
C	-4.45816	-0.13935	-0.00971	H	-3.39191	-1.04557	1.607752
C	-3.37364	-0.26987	0.850388	H	-1.42999	0.473975	1.387331
C	-2.28584	0.581094	0.731188	H	1.524085	-0.13849	-0.01981
C	-2.28047	1.593811	-0.22965	H	3.672515	-1.39579	0.183345
C	-1.08318	2.460399	-0.33162	H	7.75723	-3.83543	0.579968
C	1.21555	2.512653	-0.33649	H	9.268404	-3.61455	1.475535
C	2.483686	1.765531	-0.22047	H	9.306248	-3.83027	-0.27728
C	2.47564	0.378261	-0.05481	H	10.62335	-1.64314	-0.51831
C	3.668088	-0.31873	0.056109	H	10.58595	-1.42776	1.234572
C	4.881918	0.361736	0.002131	H	9.979264	-0.14647	0.17408
C	6.716676	-0.85021	-1.03977	H	9.409068	-2.59096	-2.10896
C	7.920317	-1.56748	-0.96421	H	8.35955	-2.19806	-4.29292
C	8.630084	-1.84999	0.354566	H	6.218289	-0.91843	-4.40379
C	8.747572	-3.37462	0.544667	H	5.192091	-0.07394	-2.34827
C	10.03979	-1.22933	0.308465	H	5.088561	0.507288	2.398935
C	8.47821	-2.03457	-2.15391	H	6.02232	0.190987	4.639487
C	7.892567	-1.81738	-3.39153	H	8.160692	-1.06447	4.932365
C	6.70237	-1.10598	-3.45104	H	9.300312	-1.96798	2.954879
C	6.120663	-0.62778	-2.2903	H	-5.28656	0.932742	-1.67124
C	6.664156	-0.55293	1.382958	H	-3.36942	2.471437	-1.87093
C	6.016245	-0.0386	2.516203	H	-3.91035	-1.61761	-1.896
C	6.545718	-0.21848	3.781778	H	-4.14678	-3.49204	-3.46074
C	7.734206	-0.91596	3.946698	H	-6.06611	-5.06406	-3.24207
C	8.371027	-1.42259	2.824335	H	-7.66017	-4.77707	-1.39725
C	7.866537	-1.26036	1.534407	H	-9.81246	-1.623	1.668908
C	-4.44556	0.848678	-0.99142	H	-10.0123	0.718082	2.380266

C	-3.36815	1.714631	-1.0967	H	-8.06421	2.248804	2.123101
C	-4.73636	-2.30822	-1.78061	H	-5.99754	1.44196	1.079586
C	-4.87461	-3.36652	-2.66592	H	-7.34437	-3.43652	2.779789
C	-5.94138	-4.24375	-2.54394	H	-5.82099	-3.00662	1.984102
C	-6.84347	-4.07263	-1.50093	H	-6.56187	-4.58411	1.665055
C	-7.79632	-1.45176	0.967268	H	0.197863	5.55526	-0.73976
C	-8.96962	-0.95683	1.528092	H	3.699025	3.517871	-0.40784
C	-9.087	0.365603	1.938099	H	5.848995	2.2606	-0.20616
C	-8.00272	1.217339	1.792244				

Table S6: Calculated XYZ coordinates of CF_3-Pym-DMAC at optimized S_1 state.

Atomic Type	Coordinates (Angstroms)			Atomic Type	Coordinates (Angstroms)		
	X	Y	X		X	Y	Z
F	-3.21636	4.36222	0.348072	C	-6.80761	0.750513	1.272967
F	-2.95732	4.737873	-1.76067	C	-6.71883	-0.5663	0.809255
F	-1.99391	6.014067	-0.32296	C	-6.74127	-3.54437	1.852362
N	-5.58184	-1.01631	0.122108	C	-1.08972	3.868887	-0.55507
N	0.076493	1.816542	-0.23255	C	0.172633	4.475155	-0.70272
N	6.125803	-0.37957	0.120421	C	-2.29425	4.721534	-0.56628
N	1.314098	3.842157	-0.62856	C	3.721422	2.423107	-0.35843
C	-8.88839	-3.69731	0.602849	C	4.905957	1.729701	-0.23972
C	-7.57348	-2.92846	0.704282	H	-9.52618	-3.30748	-0.19542
C	-6.74622	-3.02484	-0.56853	H	-9.43861	-3.64524	1.545176
C	-5.69959	-2.10324	-0.75428	H	-8.70155	-4.75697	0.413753
C	-4.4638	-0.13487	-0.01482	H	-3.37646	-1.07386	1.57022
C	-3.3659	-0.28596	0.824558	H	-1.41329	0.44928	1.348291
C	-2.27853	0.565821	0.706322	H	1.529559	-0.142	0.074179
C	-2.27185	1.594958	-0.23834	H	3.65163	-1.39741	0.292941
C	-1.06672	2.455888	-0.34902	H	7.770663	-3.83972	0.712208

C	1.239832	2.499364	-0.36635	H	9.303107	-3.57204	1.558296
C	2.468506	1.767965	-0.24368	H	9.298895	-3.87228	-0.18181
C	2.480675	0.370025	-0.00588	H	10.61382	-1.7075	-0.55952
C	3.662931	-0.3265	0.113113	H	10.61914	-1.4077	1.180563
C	4.880629	0.352302	-0.00246	H	9.999308	-0.17217	0.073704
C	6.696865	-0.9223	-1.00997	H	9.355662	-2.72339	-2.0904
C	7.911116	-1.64592	-0.93633	H	8.220546	-2.40844	-4.23692
C	8.643352	-1.86327	0.369154	H	6.084464	-1.13147	-4.34591
C	8.758973	-3.38172	0.630813	H	5.121296	-0.18767	-2.27946
C	10.05609	-1.24721	0.258759	H	5.134171	0.6053	2.322671
C	8.42716	-2.16457	-2.11723	H	6.109999	0.408028	4.58079
C	7.787474	-1.98868	-3.3362	H	8.247224	-0.83271	4.893891
C	6.590199	-1.27312	-3.39837	H	9.370629	-1.84975	2.970617
C	6.047101	-0.74434	-2.25287	H	-5.31349	0.980248	-1.63664
C	6.70362	-0.51305	1.364209	H	-3.38928	2.510894	-1.83448
C	6.060446	0.071251	2.479235	H	-3.97845	-1.58412	-1.93513
C	6.610577	-0.04336	3.732638	H	-4.25562	-3.43889	-3.52146
C	7.808515	-0.73896	3.907089	H	-6.17168	-5.01321	-3.2768
C	8.441575	-1.3136	2.813948	H	-7.7174	-4.74952	-1.38671
C	7.918245	-1.22038	1.530446	H	-9.78193	-1.63619	1.782095
C	-4.46036	0.873078	-0.97464	H	-9.95614	0.694905	2.534437
C	-3.37737	1.73356	-1.08108	H	-8.01001	2.22449	2.245939
C	-4.79962	-2.27879	-1.81091	H	-5.97476	1.427674	1.130869
C	-4.96257	-3.32465	-2.706	H	-7.28688	-3.46591	2.798
C	-6.02746	-4.20314	-2.57017	H	-5.78616	-3.02586	1.965041
C	-6.90234	-4.04468	-1.50225	H	-6.53633	-4.59974	1.646325
C	-7.78567	-1.45693	1.026114	H	0.223627	5.546927	-0.88066
C	-8.9418	-0.96923	1.627821	H	3.720031	3.490145	-0.54387
C	-9.0443	0.346773	2.061534	H	5.855508	2.248909	-0.33031

C	-7.96103	1.197712	1.8984				

Table S7: Calculated XYZ coordinates of CF_3-Pym-DMAC at optimized T_1 state.

Atomic Type	Coordinates (Angstroms)			Atomic Type	Coordinates (Angstroms)		
	X	Y	X		X	Y	X
F	-3.20127	4.361537	0.071412	C	-6.79133	0.8748	1.241035
F	-2.94877	4.59962	-2.05861	C	-6.71759	-0.47406	0.878059
F	-1.98357	5.966553	-0.70816	C	-6.76324	-3.36676	2.139676
N	-5.58812	-0.98663	0.221789	C	-1.0794	3.810814	-0.80886
N	0.084827	1.782001	-0.3657	C	0.18135	4.408378	-0.99903
N	6.125561	-0.38536	0.107557	C	-2.28754	4.66329	-0.86889
N	1.322132	3.778064	-0.89287	C	3.731742	2.383695	-0.54416
C	-8.91891	-3.58931	0.915555	C	4.911677	1.700925	-0.37536
C	-7.59572	-2.82876	0.953289	H	-9.5572	-3.2533	0.09359
C	-6.77688	-3.02764	-0.31296	H	-9.46326	-3.46159	1.854025
C	-5.72184	-2.13398	-0.57226	H	-8.74389	-4.662	0.805035
C	-4.46438	-0.12774	0.014	H	-3.38209	-0.94576	1.667796
C	-3.36731	-0.21867	0.862924	H	-1.41099	0.544996	1.328667
C	-2.27542	0.615676	0.678911	H	1.533042	-0.15204	0.066343
C	-2.2659	1.567887	-0.34261	H	3.654905	-1.394	0.344581
C	-1.05826	2.414689	-0.51723	H	7.826791	-3.55028	1.565735
C	1.249012	2.455421	-0.54762	H	9.481718	-3.11968	2.024875
C	2.474545	1.734785	-0.38412	H	9.182774	-3.97343	0.508319
C	2.484892	0.349331	-0.05784	H	10.44025	-2.13802	-0.76274
C	3.664448	-0.33799	0.091739	H	10.72978	-1.27876	0.752314
C	4.891422	0.331931	-0.0591	H	9.944513	-0.44613	-0.59897
C	6.523454	-1.28014	-0.87017	H	8.936227	-3.52535	-1.64849
C	7.711773	-2.0313	-0.7285	H	7.515068	-3.81251	-3.62296
C	8.645607	-1.85739	0.450419	H	5.462366	-2.4245	-3.89013

C	8.791421	-3.20892	1.18318	H	4.85189	-0.80205	-2.14083
C	10.02465	-1.40021	-0.07295	H	5.436001	1.18204	2.087121
C	8.031478	-2.9343	-1.73579	H	6.768951	1.672293	4.099172
C	7.2325	-3.09761	-2.8586	H	8.981679	0.56885	4.41195
C	6.081242	-2.32528	-3.00618	H	9.797701	-1.02803	2.74307
C	5.731443	-1.42042	-2.03083	H	-5.30877	0.859965	-1.69111
C	6.887249	-0.16558	1.24192	H	-3.37661	2.361187	-2.00802
C	6.403523	0.721552	2.228266	H	-4.00172	-1.72318	-1.79732
C	7.151432	0.987019	3.351937	H	-4.30816	-3.68691	-3.23981
C	8.386752	0.365466	3.528836	H	-6.23923	-5.21733	-2.86916
C	8.84651	-0.53456	2.57796	H	-7.77067	-4.79753	-0.99609
C	8.120795	-0.8285	1.429319	H	-9.78513	-1.43724	1.942735
C	-4.45603	0.801178	-1.0227	H	-9.93281	0.945202	2.518752
C	-3.36901	1.645418	-1.19574	H	-7.97443	2.429723	2.106084
C	-4.83	-2.39696	-1.6174	H	-5.95331	1.531697	1.044467
C	-5.00915	-3.50455	-2.43167	H	-7.30296	-3.2136	3.079479
C	-6.08239	-4.35867	-2.22546	H	-5.80244	-2.8513	2.20967
C	-6.94914	-4.11198	-1.16772	H	-6.56978	-4.4364	2.0109
C	-7.79146	-1.33533	1.166017	H	0.232223	5.467163	-1.24176
C	-8.93949	-0.79222	1.734849	H	3.729741	3.434287	-0.80658
C	-9.02703	0.553616	2.06882	H	5.862278	2.209458	-0.50583
C	-7.93696	1.37929	1.836672				

Table S8: Calculated XYZ coordinates of Ph-Pym-DMAC at optimized S_0 state.

Atomic Type	Coordinates (Angstroms)			Atomic Type	Coordinates (Angstroms)		
	X	Y	X		X	Y	X
N	-5.43554	-1.28568	0.05234	C	-4.37628	-3.79244	-2.44551
N	0.187987	1.658159	-0.20353	C	-5.42582	-4.69909	-2.39294
N	6.286015	-0.33355	0.119605	C	-6.47397	-4.45552	-1.519

N	1.333729	3.689278	-0.59725	C	-7.79465	-4.34812	1.20046
C	-8.52009	-0.38512	2.755036	C	2.630837	0.28751	-0.03384
C	-7.42679	0.460202	2.627191	C	3.845216	-0.37084	0.079755
C	-6.41492	0.15649	1.733773	C	10.24716	-1.09104	0.295772
C	-6.47156	-1.00279	0.945135	H	-9.32013	-0.15997	3.451274
C	-4.33241	-0.38739	-0.0377	H	-7.35507	1.363278	3.2245
C	-4.36490	0.669432	-0.94226	H	-5.56661	0.82278	1.640509
C	-3.29726	1.551111	-1.02285	H	-5.23274	0.792061	-1.58098
C	-2.17468	1.379229	-0.20985	H	-3.33295	2.368784	-1.73329
C	-0.99292	2.269481	-0.30776	H	3.751608	3.454128	-0.45605
C	1.299358	2.376985	-0.34528	H	5.942097	2.268666	-0.24918
C	2.592827	1.670597	-0.22547	H	9.639256	-2.50245	-2.09426
C	3.792303	2.382149	-0.30433	H	8.563144	-2.17678	-4.27656
C	5.006416	1.723168	-0.19032	H	9.546237	-3.47496	1.508916
C	5.037019	0.344761	0.002677	H	9.577619	-3.71952	-0.24066
C	6.902198	-0.82705	-1.03253	H	8.035300	-3.75021	0.628116
C	8.128007	-1.50597	-0.95512	H	5.260949	0.541659	2.392915
C	8.691683	-1.97512	-2.14128	H	6.22190	0.295597	4.631447
C	8.091091	-1.79595	-3.37783	H	8.39942	-0.88997	4.929263
C	9.013088	-3.26465	0.577789	H	9.549502	-1.7959	2.958731
C	8.854432	-1.74702	0.362831	H	5.345406	-0.11947	-2.34114
C	8.083664	-1.15756	1.538067	H	6.38261	-0.96513	-4.39134
C	6.859067	-0.48962	1.383561	H	-1.87178	5.405715	-2.39855
C	6.205475	0.026213	2.513085	H	-3.8952	6.819922	-2.38618
C	6.750483	-0.11407	3.776967	H	-5.49649	6.682108	-0.49839
C	7.960763	-0.77256	3.944698	H	-5.04595	5.133216	1.384177
C	8.603331	-1.28071	2.826307	H	-3.02041	3.725836	1.374621
C	6.291011	-0.6435	-2.28226	H	0.186652	5.377983	-0.81959
C	6.879085	-1.12232	-3.43942	H	-3.19900	-1.39833	1.471795

C	-1.06820	3.660897	-0.50641	H	-1.25868	0.156409	1.290875
C	-2.30771	4.465728	-0.51452	H	-9.42818	-2.18927	2.074396
C	-2.56424	5.351733	-1.56403	H	-8.95609	-2.21506	-1.28478
C	-3.70642	6.143177	-1.55945	H	-9.87546	-2.94316	0.04158
C	-4.60445	6.064897	-0.50282	H	-9.13642	-3.97354	-1.18819
C	-4.35312	5.192816	0.551428	H	-3.56304	-1.96968	-1.68503
C	-3.21545	4.399489	0.546797	H	-3.54041	-3.95375	-3.11821
C	0.163028	4.301578	-0.65894	H	-5.43042	-5.58279	-3.02109
C	-3.21612	-0.56839	0.773685	H	-7.2938	-5.16572	-1.47883
C	-2.14096	0.301584	0.678272	H	-7.91055	-5.28261	0.644945
C	-8.57265	-1.52901	1.973562	H	-8.64995	-4.2525	1.87478
C	-7.57135	-1.86653	1.063547	H	-6.88900	-4.42303	1.807522
C	-7.70807	-3.14371	0.243206	H	1.695864	-0.25737	0.018436
C	-8.99682	-3.06402	-0.59778	H	3.883400	-1.44483	0.226829
C	-6.51791	-3.33549	-0.6892	H	10.15736	-0.01257	0.143528
C	-5.45005	-2.42744	-0.75328	H	10.83563	-1.50359	-0.52819
C	-4.38712	-2.67022	-1.63631	H	10.80495	-1.25928	1.22094

Table S9: Calculated XYZ coordinates of Ph-Pym-DMAC at optimized S_1 state.

Atomic Type	Coordinates (Angstroms)			Atomic Type	Coordinates (Angstroms)		
	X	Y	X		X	Y	X
N	-5.43731	-1.28756	0.076429	C	-4.36542	-3.84044	-2.36462
N	0.17339	1.658331	-0.22895	C	-5.40654	-4.75607	-2.29
N	6.28643	-0.35945	0.120972	C	-6.45487	-4.50126	-1.41934
N	1.343781	3.667102	-0.82063	C	-7.7739	-4.3418	1.298987
C	-8.52873	-0.34706	2.758007	C	2.620379	0.286033	0.042022
C	-7.44152	0.503195	2.606874	C	3.822794	-0.37015	0.179863
C	-6.42786	0.18554	1.721075	C	10.24191	-1.10087	0.207639
C	-6.47503	-0.99375	0.960935	H	-9.33046	-0.10994	3.448594

C	-4.33279	-0.38618	-0.0278	H	-7.37651	1.422857	3.179299
C	-4.36488	0.659009	-0.94466	H	-5.58478	0.854869	1.606542
C	-3.29775	1.541412	-1.03512	H	-5.23305	0.775535	-1.58487
C	-2.17083	1.387179	-0.22143	H	-3.33395	2.353536	-1.75185
C	-0.98733	2.27399	-0.34307	H	3.759349	3.385373	-0.77009
C	1.312111	2.351549	-0.44547	H	5.933612	2.219286	-0.52046
C	2.563357	1.661133	-0.30197	H	9.522174	-2.77814	-1.99983
C	3.795585	2.336477	-0.5024	H	8.318058	-2.66239	-4.12845
C	5.001	1.685026	-0.3638	H	9.602134	-3.34069	1.702265
C	5.019823	0.32863	-0.02118	H	9.558929	-3.77395	-0.00891
C	6.842185	-0.97309	-0.98075	H	8.056112	-3.71902	0.926112
C	8.078784	-1.65517	-0.88826	H	5.325865	0.762293	2.267936
C	8.576816	-2.24922	-2.04105	H	6.367147	0.765435	4.507198
C	7.89802	-2.18614	-3.24994	H	8.547989	-0.3881	4.851074
C	9.026259	-3.23878	0.780029	H	9.649617	-1.51731	2.978716
C	8.853855	-1.74937	0.407268	H	5.210537	-0.3816	-2.25283
C	8.140878	-1.04082	1.537598	H	6.142634	-1.4572	-4.27053
C	6.901988	-0.38198	1.353824	H	-1.75386	5.648689	-2.34011
C	6.271567	0.26794	2.439254	H	-3.72111	7.115469	-2.23834
C	6.858107	0.26463	3.681468	H	-5.42931	6.80312	-0.46066
C	8.080355	-0.3822	3.873157	H	-5.10525	5.014912	1.233438
C	8.700945	-1.02101	2.808783	H	-3.11572	3.579165	1.16139
C	6.152673	-0.9097	-2.21315	H	0.208822	5.32994	-1.14735
C	6.67876	-1.5109	-3.33066	H	-3.19947	-1.37012	1.500475
C	-1.06691	3.67164	-0.63249	H	-1.26471	0.193234	1.302271
C	-2.27422	4.497199	-0.5959	H	-9.4235	-2.17467	2.122814
C	-2.47585	5.518983	-1.53983	H	-8.95377	-2.27762	-1.23373
C	-3.59268	6.340505	-1.48866	H	-9.86666	-2.98072	0.11046
C	-4.55246	6.165515	-0.49746	H	-9.12079	-4.03494	-1.09599

C	-4.37088	5.158688	0.446673	H	-3.56856	-1.991	-1.64593
C	-3.25186	4.342315	0.402737	H	-3.5301	-4.008	-3.03689
C	0.182829	4.269645	-0.89371	H	-5.40537	-5.6533	-2.89905
C	-3.21675	-0.55164	0.78817	H	-7.2694	-5.21668	-1.36155
C	-2.14581	0.32199	0.684255	H	-7.88272	-5.2903	0.765746
C	-8.57288	-1.51041	2.005384	H	-8.629	-4.23639	1.97237
C	-7.56931	-1.86199	1.103019	H	-6.86671	-4.39436	1.906187
C	-7.69732	-3.15944	0.313694	H	1.685621	-0.24165	0.187577
C	-8.98782	-3.11057	-0.52711	H	3.845304	-1.42423	0.44055
C	-6.50634	-3.36298	-0.61522	H	10.14474	-0.04555	-0.05702
C	-5.44641	-2.44565	-0.70008	H	10.79147	-1.60565	-0.58969
C	-4.38347	-2.70073	-1.58117	H	10.83511	-1.17245	1.121733

Table S10: Calculated XYZ coordinates of Ph-Pym-DMAC at optimized T_1 state.

Atomic	Coordinates (Angstroms)			Atomic	Coordinates (Angstroms)		
Type	X	Y	X	Type	X	Y	X
N	-6.07701	-0.78034	0.199212	C	-6.81775	-2.48044	-2.99545
N	0.091252	0.770896	-0.88053	C	-8.05953	-3.04122	-2.73128
N	6.289396	-0.71559	0.063934	C	-8.62898	-2.84225	-1.48311
N	1.121241	1.901736	-2.74649	C	-8.93772	-3.32316	1.484591
C	-7.6333	-0.09557	4.038291	C	2.635181	-0.07433	0.022169
C	-6.4001	0.427301	3.675075	C	3.87761	-0.53791	0.413908
C	-5.89462	0.197114	2.407826	C	10.25505	-1.44292	0.189967
C	-6.61108	-0.56406	1.471902	H	-8.04188	0.076794	5.02765
C	-4.80682	-0.22196	-0.12403	H	-5.82284	1.018935	4.377971
C	-4.7265	1.042739	-0.69889	H	-4.93176	0.60993	2.134203
C	-3.48968	1.589504	-1.00554	H	-5.64062	1.592648	-0.89431
C	-2.31149	0.870647	-0.75737	H	-3.43024	2.58305	-1.43735

C	-1.01456	1.434662	-1.09448	H	3.529931	1.562616	-2.81489
C	1.199434	1.189932	-1.55011	H	5.769854	0.729772	-2.09745
C	2.496251	0.68978	-1.14901	H	9.333798	-4.11118	-0.16696
C	3.641743	0.977482	-1.91013	H	7.902212	-5.44552	-1.6488
C	4.88257	0.512088	-1.51266	H	9.881758	-2.01381	2.869492
C	5.008479	-0.24578	-0.34904	H	9.638937	-3.49523	1.938109
C	6.731961	-1.96393	-0.37937	H	8.262762	-2.71765	2.735512
C	7.983945	-2.46181	0.013129	H	5.60597	1.661877	0.993505
C	8.367745	-3.71495	-0.46352	H	6.926565	3.099058	2.47182
C	7.565895	-4.47535	-1.3006	H	9.176498	2.349528	3.254521
C	9.193705	-2.53015	2.194634	H	10.0336	0.168332	2.523978
C	8.926455	-1.69124	0.929993	H	4.95188	-2.34462	-1.52936
C	8.329072	-0.35071	1.340836	H	5.678657	-4.53969	-2.33541
C	7.066076	0.081652	0.907583	H	0.021114	5.187265	-2.57505
C	6.580492	1.329231	1.328165	H	-0.05919	7.294651	-1.31634
C	7.328606	2.13953	2.163521	H	-0.98831	7.345221	0.984299
C	8.579388	1.724825	2.599687	H	-1.82635	5.253006	2.020984
C	9.055454	0.491614	2.182069	H	-1.75318	3.133958	0.776612
C	5.917382	-2.73023	-1.2268	H	-0.1416	3.025343	-3.90095
C	6.330295	-3.97014	-1.68096	H	-3.71845	-1.92838	0.581559
C	-0.85165	2.775258	-1.74954	H	-1.49169	-0.96201	-0.00441
C	-0.85679	3.990416	-0.99773	H	-9.30317	-1.2536	3.395461
C	-0.3839	5.196629	-1.56863	H	-9.90935	-0.24053	0.208262
C	-0.42931	6.382167	-0.86076	H	-10.5903	-1.10919	1.592571
C	-0.94953	6.411614	0.433713	H	-10.6926	-1.81096	-0.0255
C	-1.42317	5.235215	1.013858	H	-5.20182	-1.30533	-2.24011
C	-1.38361	4.042886	0.314947	H	-6.3435	-2.6192	-3.9614
C	0.059897	2.601104	-2.91805	H	-8.57794	-3.6257	-3.48302
C	-3.639	-0.94266	0.135786	H	-9.59958	-3.2825	-1.27771

C	-2.40568	-0.40766	-0.18306	H	-9.5542	-3.94416	0.829191
C	-8.33849	-0.84609	3.110195	H	-9.45111	-3.24188	2.446418
C	-7.8595	-1.09871	1.82509	H	-7.98807	-3.83875	1.647853
C	-8.70044	-1.93219	0.865503	H	1.750626	-0.29155	0.608822
C	-10.055	-1.23081	0.647035	H	3.990535	-1.12804	1.31706
C	-8.0056	-2.09998	-0.48048	H	10.08769	-0.84831	-0.71158
C	-6.75193	-1.53652	-0.76287	H	10.72136	-2.38651	-0.106
C	-6.17095	-1.73719	-2.02405	H	10.9636	-0.90541	0.825969

4. Thermal and electrical properties

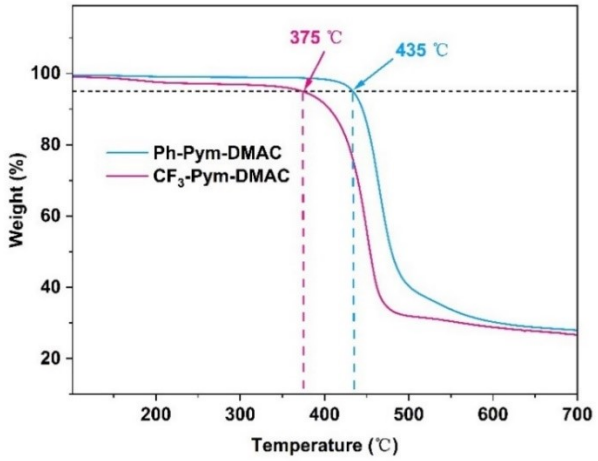


Figure S1. TGA curves of CF_3-Pym-DMAC and Ph-Pym-DMAC. The black dashed line marks loss 5% of the original sample weight.

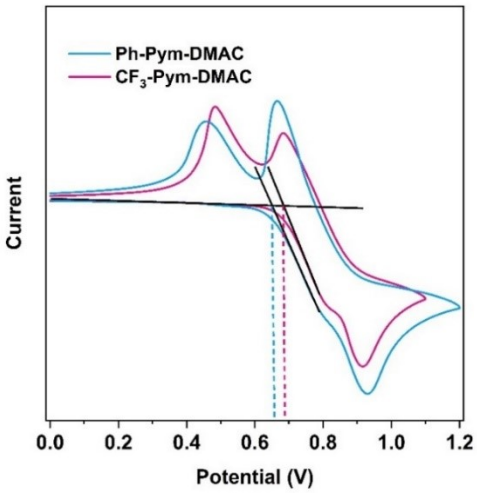


Figure S2. Cyclic voltammograms for the oxidation of CF_3-Pym-DMAC and Ph-Pym-DMAC in DCM at RT.

Cyclic voltammetry was performed at room temperature in anhydrous and argon-saturated dichloromethane (DCM) solutions of 0.1 M tetrabutylammonium hexafluorophosphate and 1.0 mM investigated compounds with a CHI660 electrochemical analyzer. Glassy carbon as the working electrode, platinum wire was selected as auxiliary electrode and Ag/Ag^+ (0.01 M of $AgNO_3$ in acetonitrile), ferrocene was used to be reference electrode and internal standard, respectively. The HOMO and LUMO energy levels were calculated according to the equation: $E_{HOMO} = - [E_{ox} - E_{Fc/Fc+} + 4.8]$ eV, $E_g = 1241/ \lambda_{onset}$, $E_{LUMO} = E_{HOMO} + E_g$. The HOMO and LUMO energy levels were estimated from the cyclic voltammetry and optical bandgaps (E_g) determined from the onset of the absorption band (λ_{onset}). Based on the above formulas, HOMO/LUMO energy levels of CF_3-Pym-DMAC and Ph-Pym-DMAC were calculated to be -5.27/-2.50 eV and -5.23/-2.28 eV, respectively.

Table S11. Summary of T_d, CV data and energy levels.

	T_d[a] [°C]	E_{ox}[b] [eV]	$E_{Fc/Fc+}$[b] [eV]	E_g[b] [eV]	E_{HOMO}[b] [eV]	E_{LUMO}[b] [eV]
CF_3-Pym-DMAC	375	0.69	0.22	2.77	-5.27	-2.50
Ph-Pym-DMAC	435	0.65	0.22	2.95	-5.23	-2.28

[a] Thermal decomposition temperature corresponding to 5% weight loss. [b] HOMO levels were calculated from the oxidation onset potentials in CV curves. LUMO levels estimated by the empirical equation $E_{LUMO} = E_{HOMO} + E_g$.

5. Photophysical Properties

Steady-state photoluminescence spectra were measured on the FLS980 in Edinburgh with a xenon lamp as the excitation light source. The life test uses the NT242-1K OPO laser as the light source, and the photoluminescence attenuation curve is measured in time-dependent single-photon counting mode on the FLS980 in Edinburgh, and the final lifetime is obtained by fitting the attenuation curve. The low-temperature time-resolved spectroscopy test was tested on the Lincoln heating table to 77 K, and the NT242-1K OPO laser was used as the excitation source, and the time-resolved

photoluminescence spectrum was tested on the LP980 spectrophotometer in Edinburgh. Rate constants of the investigated compounds in 20 wt% BCPO films at room temperature are determined from the measured quantum yields and lifetimes of the prompt fluorescence (PF) and delayed fluorescence (DF) components according to equations S1-S6.[3]

$$k_{PF} = \frac{1}{\tau_{PF}}$$ Equation S1

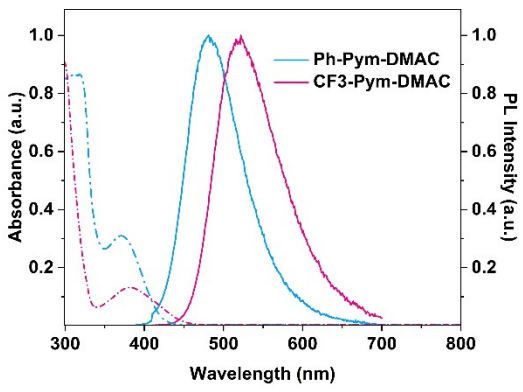
$$k_{DF} = \frac{1}{\tau_{DF}}$$ Equation S2

$$k_{RISC} = \frac{k_{PF} + k_{DF}}{2} - \sqrt{\left(\frac{k_{PF} + k_{DF}}{2}\right)^2 - k_{PF}k_{DF}\left(1 + \frac{\emptyset_{DF}}{\emptyset_{PF}}\right)}$$ Equation S3

$$k_{ISC} = \frac{k_{PF}k_{DF}\emptyset_{DF}}{k_{RISC}\ \emptyset_{PF}}$$ Equation S4

$$k_r^S \approx \frac{k_{PF}k_{DF}}{k_{RISC}}\emptyset_{PL}$$ Equation S5

$$k_{nr}^S \approx \frac{k_{PF}k_{DF}}{k_{RISC}}(1 - \emptyset_{PL})$$ Equation S6



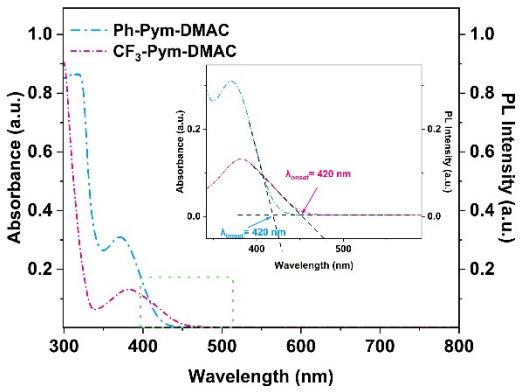


Figure S3. Left: UV-vis absorption spectra of CF_3-Pym-DMAC and Ph-Pym-DMAC in diluted toluene solutions (1×10^{-5} M); Right: PL spectra of CF_3-Pym-DMAC and Ph-Pym-DMAC in 20 wt%-doped BCPO films at room temperature (excited at 410 nm).

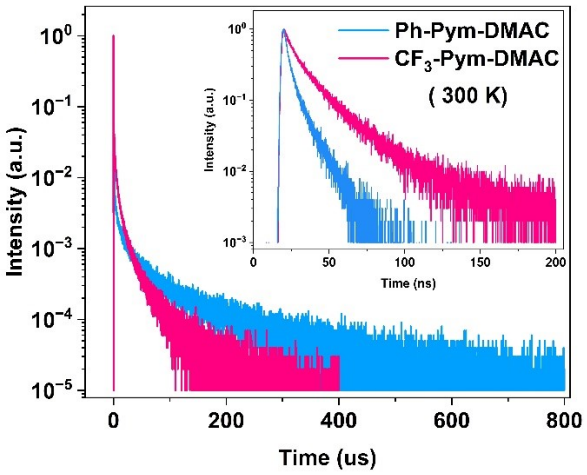


Figure S4. Temperature-dependent transient PL spectra with films in vacuum-deposited 20 wt%-doped BCPO host at 300 K.

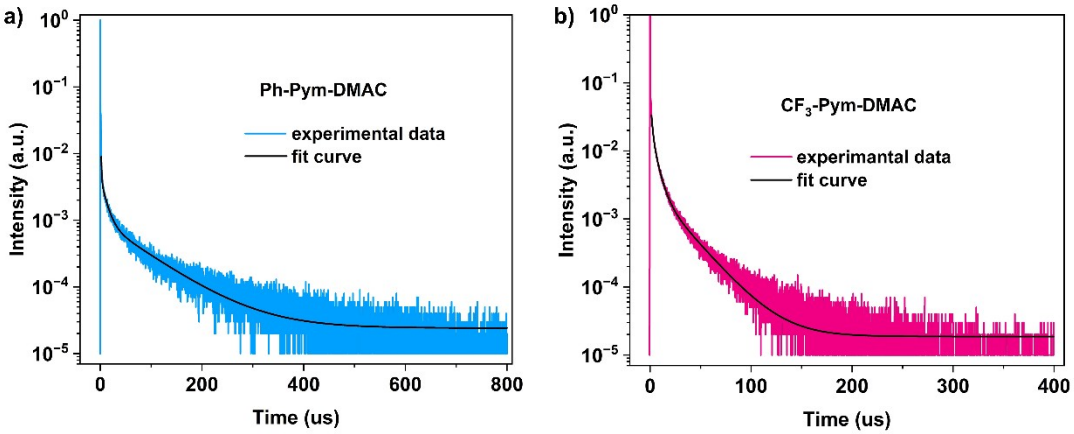


Figure S5. Transient PL decay curves of Ph-Pym-DMAC and CF_3-Pym-DMAC in 20 wt% doped in BCPO at 300 K. The black line indicates the fitting curve.

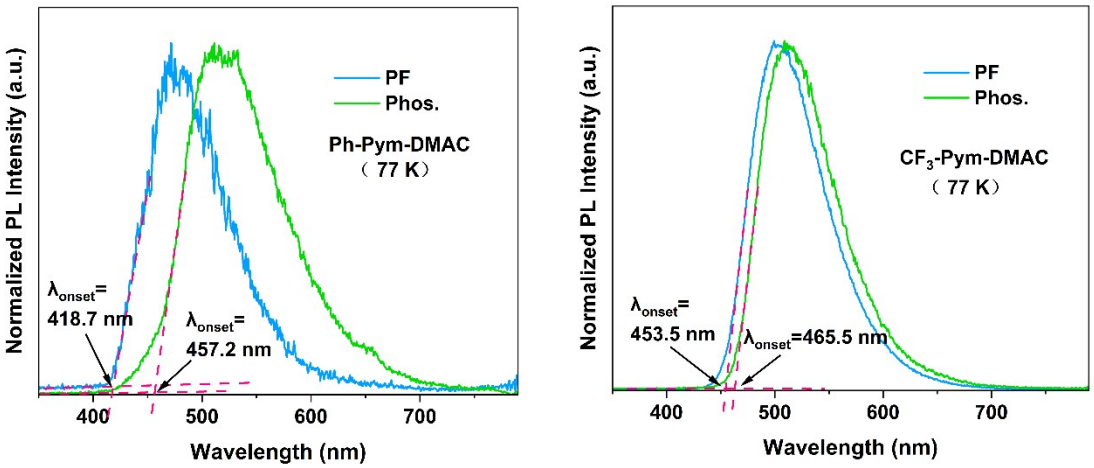


Figure S6. Time-resolved PL spectra in the 20 wt%-doped BCPO films at 77 K. The intersections of red tangent lines indicate the onset wavelengths.

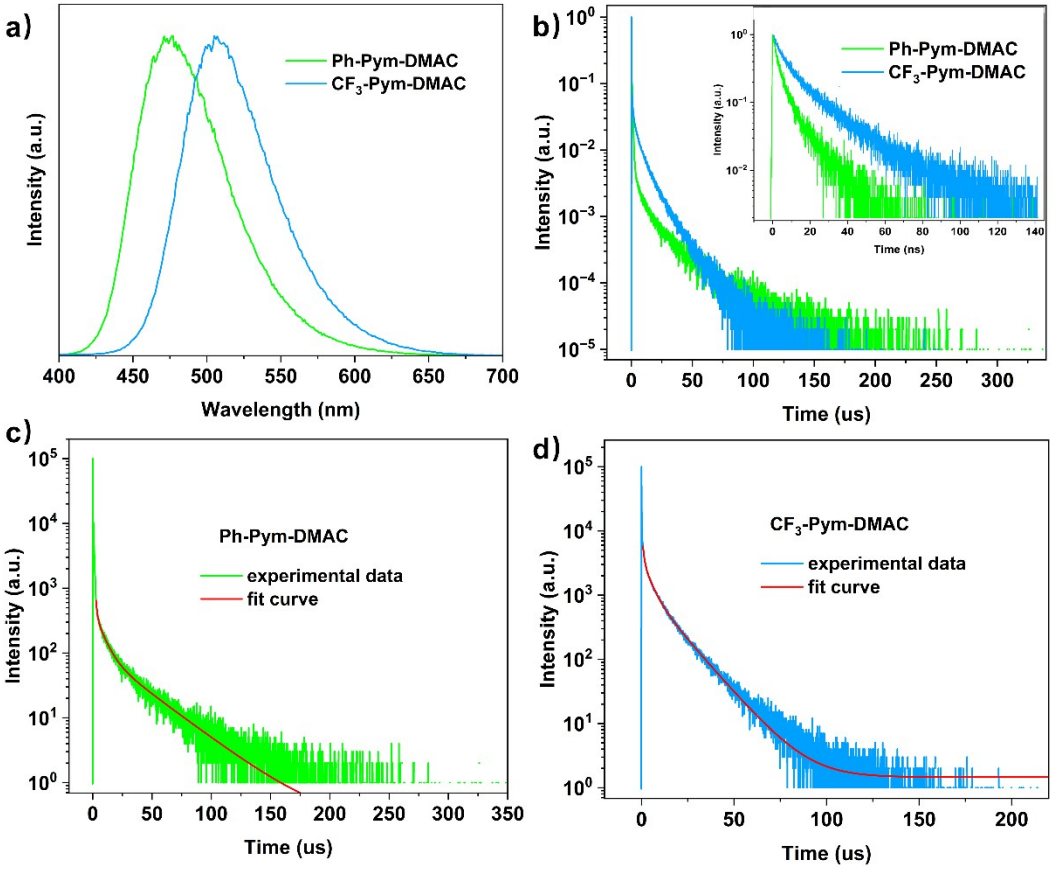


Figure S7. a) Steady-state photoluminescence spectra of Ph-Pym-DMAC and CF_3-Pym-DMAC in non-doped films at 300 K (excited at 380 nm); Transient PL decay curves of Ph-Pym-DMAC and CF_3-Pym-DMAC in non-doped films at 300 K; the inset shows the corresponding fractional contributions of prompt fluorescence and delayed fluorescence; c/d) Transient PL decay curves of

Ph-Pym-DMAC and CF_3-Pym-DMAC in non-doped films at 300 K; The black line indicates the fitting curve.

Table S12. Photophysical data of CF_3-Pym-DMAC and Ph-Pym-DMAC in neat films.

Compound	λ_{PL}[a] nm	$\Phi_{PL}/\Phi_{PF}/\Phi_{DF}$[b] %	τ_{PF}/τ_{DF}[c] ns/μs	k_r^s/k_{nr}^s[e] $10^7 s^{-1}$	k_{ISC}/k_{RISC}[f] $10^7/10^5\ s^{-1}$
Ph-Pym-DMAC	475	24/18/6	8.4/19.9	2.17/6.88	2.80/0.66
CF_3-Pym-DMAC	505	79/22/57	15.3/8.6	1.35/0.38	4.76/4.38

Measured in 20 wt% doped BCPO films: [a] PL emission peak (excited at 335 nm); [b] Overall PLQY ; Φ_{PF} and Φ_{DF} are the quantum yields of prompt fluorescence and delayed fluorescence, respectively; [c] Fluorescence lifetimes of prompt (τ_{PF}) and delayed (τ_{DF}) components evaluated at 300 K; [d] Determined from the onset of fluorescence/phosphorescence spectrum at 77 K; [e] Rate constants of radiative and nonradiative of S_1 states, respectively; [f] Rate constants of intersystem crossing (ISC) and reverse ISC, respectively.

Table S13. Key photophysical properties of pyrimidine and methylacridine based emitters.

Emitter	λ_{EL} nm	k_{RISC} $10^5\ s^{-1}$	τ_d μs	EQE %	Ref.
CF3-Pym-DMAC	510	5.84	10.2	25.0	This work
Ac-PPM	458	0.11	78	11.4	4
T3	464	0.74	24.5	14.2	5
T4	476	7.39	61.5	11.8	5
22bpmAc	517	0.43	37.5	15.7	6
25bpmAc	524	0.92	17.1	20.5	6
55bpmAc	512	0.79	21.8	24.9	6
AcPYM	487	0.01	486	11.9	7
AcRPyr	475	57	1.76	14.3	8
23AcCz-PM	499	1.8	3.4	28.4	9

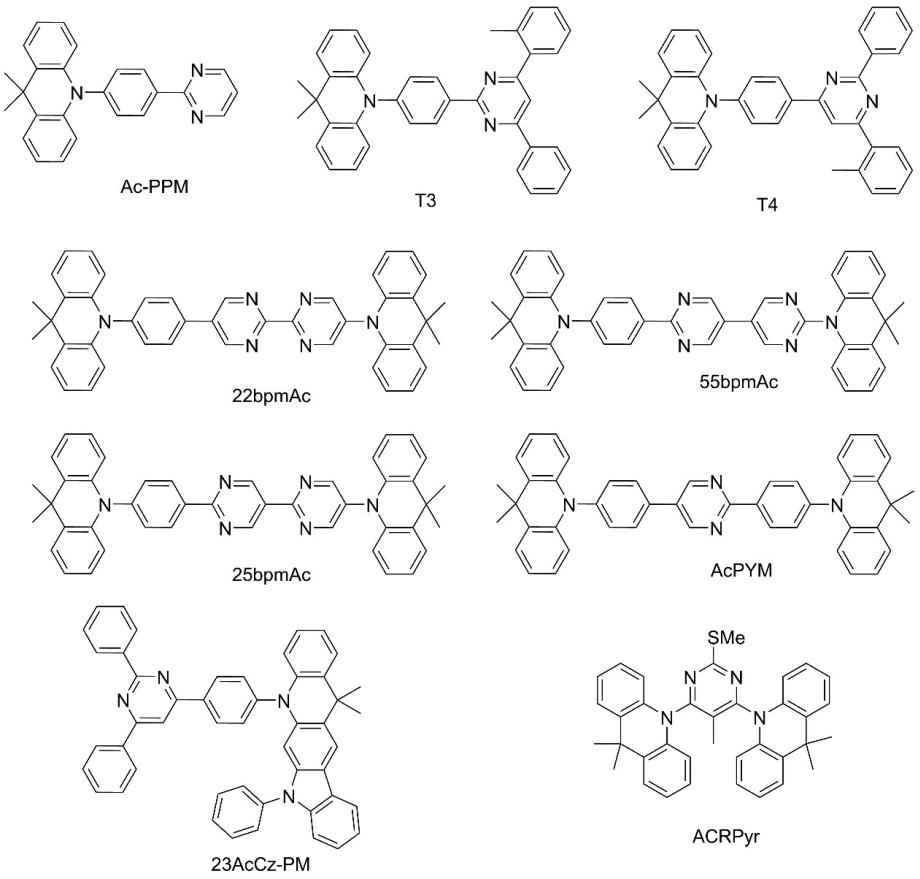


Figure S8. The structures of emitters base on pyrimidine and methylacridine.

6. Device Fabrication and Characterization

The indium tin oxide (ITO) glass surface was ultrasonically cleaned with detergent, deionized water, acetone and ethanol for 15 minutes, and then the cleaned sheets were purged with dry nitrogen to remove the solvent on the surface, and finally treated with ultraviolet ozone for 15 minutes. The organic materials including TAPC, mCP, DPEPO, TmPyPB, and the EML of the multilayer device is sequentially deposited onto ITO glass at a base pressure less than 2×10^{-5} Pa by thermal evaporation in a vacuum chamber at a rate of 1 Å/s^{-1}, and inorganic layers (Liq and Al) were under 4×10^{-4} Pa at a rate of 0.1 and 5 Å/s^{-1}, respectively. The electroluminescence (EL) spectra, Commission Internatinale de L'Eclairage coordinates (CIE), current density-voltage (J-V) curves, and luminance-voltage (L-V) curves of the device were measured using the TOPCON SR-UL1R spectroradiometer and the Keithley 2400 source meter.

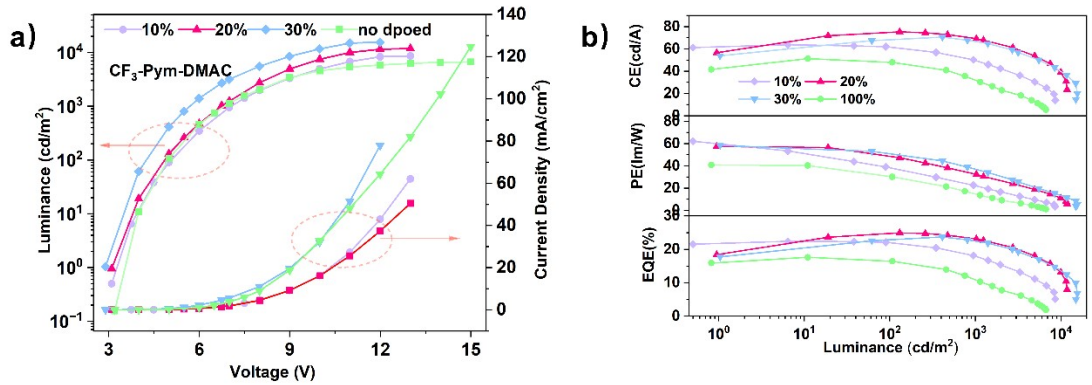


Figure S9. [a] Current density−voltage−luminance characteristics; [b] external quantum efficiency (EQE), current efficiency (CE) and power efficiency (PE) - luminance curves.

Table S14. The important characteristics of device.

CF_3-Pym-DMAC	λ_{EL}[a]	L_{max}[b]	V_{on}[c]	EQE[d]	CE[e]	PE[e]	CIE[f]
	[nm]	[cd/m^2]	[V]	[%]	[cd/A]	[lm/W]	[x,y]
10%	507	8614	3.3	22.3/22.0/18.0	63.7	62.1	0.27,0.51
20%	510	11820	3.1	25.0/24.8/23.2	75.3	57.3	0.28,0.55
30%	511	15610	2.9	23.7/22.9/22.4	70.6	58.3	0.30,0.55
100%	505	6687	3.5	17.6/16.5/10.9	51.2	40.8	0.28,0.53

[a] record at maximum EQE; [b] maximum luminance [c] V_{on}, the turn-on voltage recorded at 1 cd/m^2; [d] EQE maximum value, value at 100 cd/m^2 and value at 1000 cd/m^2; [e] maximum current efficiency and maximum power efficiency; [f] Commission Internatinale de L'Eclairage coordinates measured.

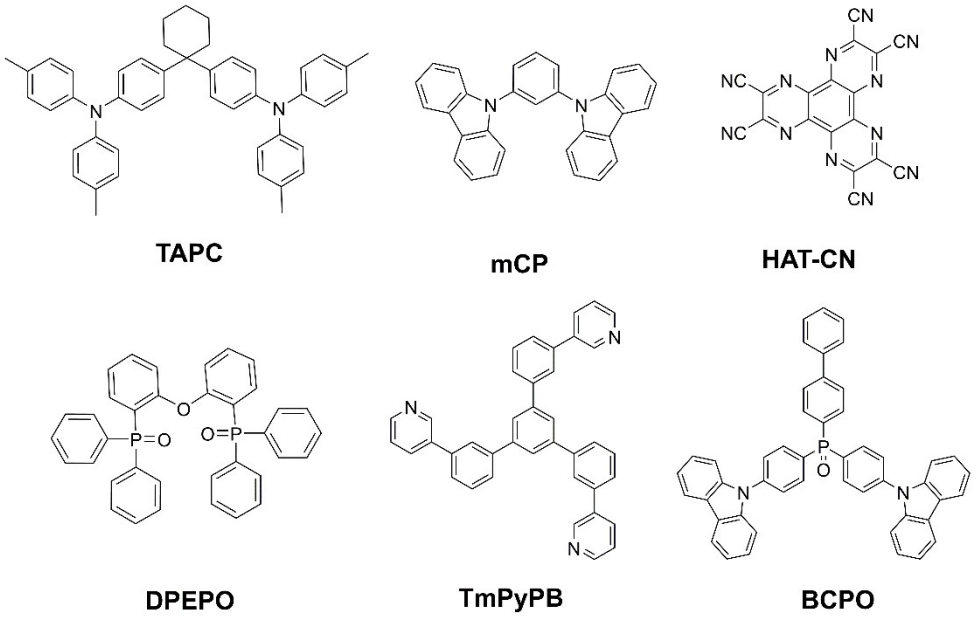


Figure S10. The Molecular structures of materials used in OLEDs.

7. Structural characteristics

The crystals of CF_3-Pym-DMAC and Ph-Pym-DMAC were obtained by diffusion method at room temperature, further confirming the exact configurations by single-crystal X-ray diffraction. The single crystal was collected at 200 K by Bruker's diffraction data on the D8 VENTRUE diffractometer, and the X-ray source used Kα radiation from the mammolybdenum target (λ = 0.71073 Å). The crystal structure is resolved by direct method and differential Fourier synthesis method. Finally, it was checked by check cif and there were no class A errors.

Table S15. Crystal data and structure refinements.

Compounds	CF_3-Pym-DMAC	Ph-Pym-DMAC
Empirical formula	$C_{47}H_{37}N_4F_3$	$C_{52}H_{42}N_4$
Formula weight	714.80	722.89
Temperature/K	200.00	200.00
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	19.5350(10)	16.1698(7)
b/Å	8.1840(4)	8.0307(3)
c/Å	23.4718(12)	30.1569(13)
α/°	90	90
β/°	93.966(2)	97.3910(10)
γ/°	90	90
Volume/Å^3	3743.6(3)	3883.5(3)
Z	4	4
ρ_{calc}g/cm^3	1.268	1.236
μ/mm^{-1}	0.085	0.072
F(000)	1496.0	1528.0
Crystal size/mm^3	0.4 × 0.3 × 0.2	0.4 × 0.4 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for	5.25 to 50.036	3.956 to 55.07

data collection/°		
Index ranges	$-23 \le h \le 23$, $-9 \le k \le 9$, $-27 \le l \le 27$	$-21 \le h \le 20$, $-10 \le k \le 10$, $-39 \le l \le 39$
Reflections collected	54658	44362
Independent reflections	6591 [R_{int} = 0.0919, R_{sigma} = 0.0452]	8921 [R_{int} = 0.0814, R_{sigma} = 0.0611]
Data/restraints/parameters	6591/0/482	8921/0/509
Goodness-of-fit on F^2	1.040	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0680, wR_2 = 0.1778	R_1 = 0.0658, wR_2 = 0.1640
Final R indexes [all data]	R_1 = 0.1050, wR_2 = 0.2112	R_1 = 0.1247, wR_2 = 0.2060
Largest diff. peak/hole / e $Å^{-3}$	1.20/-0.60	0.43/-0.25

Table S16. Bond Lengths for CF_3-Pym-DMAC.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C45	1.329(5)	C13	C14	1.387(5)
F2	C45	1.327(4)	C14	C47	1.384(5)
F3	C45	1.336(4)	C15	C16	1.398(4)
N1	C4	1.419(4)	C15	C23	1.393(4)
N1	C5	1.438(4)	C16	C17	1.528(5)
N1	C41	1.424(4)	C16	C20	1.396(5)
N2	C9	1.337(4)	C17	C18	1.606(7)
N2	C10	1.343(4)	C17	C19	1.452(7)
N3	C14	1.438(4)	C17	C29	1.500(5)
N3	C15	1.408(4)	C20	C21	1.385(5)
N3	C24	1.400(4)	C21	C22	1.373(5)

N4	C10	1.330(4)	C22	C23	1.376(5)
N4	C44	1.330(4)	C24	C25	1.393(5)
C1	C2	1.538(5)	C24	C29	1.399(5)
C2	C3	1.521(4)	C25	C26	1.380(6)
C2	C36	1.516(5)	C26	C27	1.380(6)
C2	C42	1.553(5)	C27	C28	1.371(6)
C3	C4	1.403(4)	C28	C29	1.401(5)
C3	C35	1.386(5)	C30	C31	1.380(4)
C4	C32	1.395(4)	C32	C33	1.388(5)
C5	C6	1.377(4)	C33	C34	1.379(5)
C5	C30	1.387(4)	C34	C35	1.383(5)
C6	C7	1.381(5)	C36	C37	1.401(4)
C7	C8	1.382(4)	C36	C41	1.407(4)
C8	C9	1.485(4)	C37	C38	1.369(5)
C8	C31	1.384(4)	C38	C39	1.380(5)
C9	C43	1.397(5)	C39	C40	1.386(5)
C10	C11	1.492(4)	C40	C41	1.389(4)
C11	C12	1.390(4)	C43	C44	1.374(5)
C11	C46	1.391(4)	C43	C45	1.503(5)
C12	C13	1.390(4)	C46	C47	1.386(5)

Table S17. Bond Angles for CF_3-Pym-DMAC.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C4	C32	C33	-175.2(3)	C14	N3	C24	C29	-173.8(3)
N1	C5	C6	C7	-180.0(3)	C15	N3	C14	C13	84.1(4)
N1	C5	C30	C31	178.3(3)	C15	N3	C14	C47	-93.5(4)
N2	C9	C43	C44	1.3(5)	C15	N3	C24	C25	-170.1(3)
N2	C9	C43	C45	-176.9(3)	C15	N3	C24	C29	8.5(5)
N2	C10	C11	C12	2.9(5)	C15	C16	C17	C18	132.0(4)

N2	C10	C11	C46	180.0(3)	C15	C16	C17	C19	-109.7(4)
N3	C14	C47	C46	175.4(3)	C15	C16	C17	C29	14.2(5)
N3	C15	C16	C17	-4.2(5)	C15	C16	C20	C21	0.7(5)
N3	C15	C16	C20	177.8(3)	C16	C15	C23	C22	1.3(5)
N3	C15	C23	C22	-178.3(3)	C16	C17	C29	C24	-13.8(5)
N3	C24	C25	C26	178.5(4)	C16	C17	C29	C28	168.2(4)
N3	C24	C29	C17	3.4(5)	C16	C20	C21	C22	1.0(6)
N3	C24	C29	C28	-178.5(3)	C17	C16	C20	C21	-177.3(4)
N4	C10	C11	C12	-175.7(3)	C18	C17	C29	C24	-132.0(4)
N4	C10	C11	C46	1.3(5)	C18	C17	C29	C28	50.0(5)
C1	C2	C3	C4	167.6(3)	C19	C17	C29	C24	110.4(5)
C1	C2	C3	C35	-15.6(5)	C19	C17	C29	C28	-67.6(5)
C1	C2	C36	C37	15.2(4)	C20	C16	C17	C18	-50.1(5)
C1	C2	C36	C41	-168.5(3)	C20	C16	C17	C19	68.2(5)
C2	C3	C4	N1	-10.0(4)	C20	C16	C17	C29	-167.9(3)
C2	C3	C4	C32	171.1(3)	C20	C21	C22	C23	-1.5(6)
C2	C3	C35	C34	-173.1(3)	C21	C22	C23	C15	0.4(5)
C2	C36	C37	C38	172.0(3)	C23	C15	C16	C17	176.2(3)
C2	C36	C41	N1	11.6(4)	C23	C15	C16	C20	-1.8(5)
C2	C36	C41	C40	-169.1(3)	C24	N3	C14	C13	-93.6(4)
C3	C2	C36	C37	139.1(3)	C24	N3	C14	C47	88.8(4)
C3	C2	C36	C41	-44.7(4)	C24	N3	C15	C16	-8.0(5)
C3	C4	C32	C33	3.8(5)	C24	N3	C15	C23	171.5(3)
C4	N1	C5	C6	-102.1(3)	C24	C25	C26	C27	0.6(8)
C4	N1	C5	C30	77.7(4)	C25	C24	C29	C17	-178.0(4)
C4	N1	C41	C36	26.7(4)	C25	C24	C29	C28	0.1(5)
C4	N1	C41	C40	-152.6(3)	C25	C26	C27	C28	-1.0(9)
C4	C3	C35	C34	3.7(5)	C26	C27	C28	C29	1.0(8)
C4	C32	C33	C34	0.9(5)	C27	C28	C29	C17	177.6(4)

C5	N1	C4	C3	-177.6(3)	C27	C28	C29	C24	-0.5(6)
C5	N1	C4	C32	1.4(4)	C29	C24	C25	C26	-0.1(6)
C5	N1	C41	C36	176.9(3)	C30	C5	C6	C7	0.2(5)
C5	N1	C41	C40	-2.4(4)	C31	C8	C9	N2	-119.7(3)
C5	C6	C7	C8	1.8(5)	C31	C8	C9	C43	60.9(4)
C5	C30	C31	C8	1.6(5)	C32	C33	C34	C35	-3.2(5)
C6	C5	C30	C31	-1.9(5)	C33	C34	C35	C3	0.9(5)
C6	C7	C8	C9	179.6(3)	C35	C3	C4	N1	173.0(3)
C6	C7	C8	C31	-2.2(5)	C35	C3	C4	C32	-5.9(4)
C7	C8	C9	N2	58.5(4)	C36	C2	C3	C4	43.8(4)
C7	C8	C9	C43	-120.9(4)	C36	C2	C3	C35	-139.4(3)
C7	C8	C31	C30	0.4(5)	C36	C37	C38	C39	-1.7(5)
C8	C9	C43	C44	-179.3(3)	C37	C36	C41	N1	-171.8(3)
C8	C9	C43	C45	2.5(5)	C37	C36	C41	C40	7.5(4)
C9	N2	C10	N4	2.2(5)	C37	C38	C39	C40	4.5(5)
C9	N2	C10	C11	-176.3(3)	C38	C39	C40	C41	-1.2(5)
C9	C8	C31	C30	178.7(3)	C39	C40	C41	N1	174.4(3)
C9	C43	C44	N4	0.3(6)	C39	C40	C41	C36	-4.9(5)
C9	C43	C45	F1	46.0(5)	C41	N1	C4	C3	-27.5(4)
C9	C43	C45	F2	-74.4(5)	C41	N1	C4	C32	151.4(3)
C9	C43	C45	F3	164.9(3)	C41	N1	C5	C6	107.8(3)
C10	N2	C9	C8	178.1(3)	C41	N1	C5	C30	-72.4(4)
C10	N2	C9	C43	-2.5(4)	C41	C36	C37	C38	-4.3(4)
C10	N4	C44	C43	-0.7(6)	C42	C2	C3	C4	-72.8(3)
C10	C11	C12	C13	174.2(3)	C42	C2	C3	C35	104.0(4)
C10	C11	C46	C47	-174.5(3)	C42	C2	C36	C37	-104.5(3)
C11	C12	C13	C14	0.7(5)	C42	C2	C36	C41	71.7(3)
C11	C46	C47	C14	-0.1(5)	C44	N4	C10	N2	-0.5(6)
C12	C11	C46	C47	2.6(5)	C44	N4	C10	C11	178.0(3)

C12	C13	C14	N3	-175.7(3)	C44	C43	C45	F1	-132.2(4)
C12	C13	C14	C47	1.9(5)	C44	C43	C45	F2	107.4(4)
C13	C14	C47	C46	-2.2(5)	C44	C43	C45	F3	-13.2(5)
C14	N3	C15	C16	174.3(3)	C45	C43	C44	N4	178.6(4)
C14	N3	C15	C23	-6.2(5)	C46	C11	C12	C13	-2.9(5)
C14	N3	C24	C25	7.6(5)					

Table S18. Bond Lengths for Ph-Pym-DMAC.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C4	1.400(3)	C18	C28	1.377(4)
N1	C5	1.442(3)	C19	C20	1.542(4)
N1	C44	1.404(3)	C20	C21	1.524(3)
N2	C9	1.344(3)	C20	C52	1.559(3)
N2	C10	1.342(3)	C21	C22	1.400(3)
N3	C14	1.444(3)	C21	C26	1.397(3)
N3	C15	1.409(3)	C22	C23	1.403(3)
N3	C22	1.400(3)	C23	C24	1.374(3)
N4	C10	1.345(3)	C24	C25	1.380(4)
N4	C36	1.331(3)	C25	C26	1.377(4)
C1	C2	1.385(4)	C27	C28	1.380(3)
C1	C39	1.375(4)	C29	C30	1.480(4)
C2	C3	1.374(4)	C29	C36	1.389(4)
C3	C4	1.397(3)	C30	C31	1.379(4)
C4	C40	1.403(3)	C30	C35	1.398(4)
C5	C6	1.380(4)	C31	C32	1.386(5)
C5	C37	1.383(3)	C32	C33	1.360(6)
C6	C7	1.382(3)	C33	C34	1.368(5)
C7	C8	1.403(3)	C34	C35	1.389(4)
C8	C9	1.490(3)	C37	C38	1.381(3)

C8	C38	1.376(3)	C39	C40	1.399(4)
C9	C29	1.402(4)	C40	C41	1.521(4)
C10	C11	1.480(3)	C41	C42	1.546(3)
C11	C12	1.390(3)	C41	C43	1.518(4)
C11	C50	1.394(4)	C41	C49	1.548(4)
C12	C13	1.387(3)	C43	C44	1.399(3)
C13	C14	1.383(3)	C43	C48	1.394(4)
C14	C51	1.382(3)	C44	C45	1.399(4)
C15	C16	1.402(3)	C45	C46	1.380(4)
C15	C27	1.398(3)	C46	C47	1.379(4)
C16	C17	1.390(3)	C47	C48	1.365(4)
C16	C20	1.522(3)	C50	C51	1.387(3)
C17	C18	1.378(4)			

Table S19. Bond Angles for Ph-Pym-DMAC.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	N1	C5	118.3(2)	C21	C20	C52	109.3(2)
C4	N1	C44	122.0(2)	C22	C21	C20	122.9(2)
C44	N1	C5	119.67(19)	C26	C21	C20	120.0(2)
C10	N2	C9	117.8(2)	C26	C21	C22	117.1(2)
C15	N3	C14	119.07(18)	N3	C22	C23	120.0(2)
C22	N3	C14	118.10(18)	C21	C22	N3	120.0(2)
C22	N3	C15	121.25(18)	C21	C22	C23	120.0(2)
C36	N4	C10	115.6(2)	C24	C23	C22	120.7(2)
C39	C1	C2	119.2(3)	C23	C24	C25	120.4(2)
C3	C2	C1	119.5(3)	C26	C25	C24	118.8(2)
C2	C3	C4	121.8(3)	C25	C26	C21	123.1(2)
N1	C4	C40	120.0(2)	C28	C27	C15	120.4(2)
C3	C4	N1	120.7(2)	C18	C28	C27	120.2(3)

C3	C4	C40	119.3(2)	C9	C29	C30	125.0(2)
C6	C5	N1	120.4(2)	C36	C29	C9	114.9(2)
C6	C5	C37	120.0(2)	C36	C29	C30	120.1(2)
C37	C5	N1	119.5(2)	C31	C30	C29	120.3(2)
C5	C6	C7	119.7(2)	C31	C30	C35	118.6(3)
C6	C7	C8	120.2(2)	C35	C30	C29	121.1(2)
C7	C8	C9	120.9(2)	C30	C31	C32	120.9(3)
C38	C8	C7	119.1(2)	C33	C32	C31	120.2(4)
C38	C8	C9	119.9(2)	C32	C33	C34	120.1(3)
N2	C9	C8	115.4(2)	C33	C34	C35	120.7(3)
N2	C9	C29	121.6(2)	C34	C35	C30	119.5(3)
C29	C9	C8	122.9(2)	N4	C36	C29	124.7(3)
N2	C10	N4	125.1(2)	C38	C37	C5	120.3(2)
N2	C10	C11	116.8(2)	C8	C38	C37	120.3(2)
N4	C10	C11	118.0(2)	C1	C39	C40	122.8(3)
C12	C11	C10	120.5(2)	C4	C40	C41	122.8(2)
C12	C11	C50	119.2(2)	C39	C40	C4	117.5(2)
C50	C11	C10	120.3(2)	C39	C40	C41	119.7(2)
C13	C12	C11	120.4(2)	C40	C41	C42	108.8(2)
C14	C13	C12	120.1(2)	C40	C41	C49	109.5(2)
C13	C14	N3	119.9(2)	C42	C41	C49	108.7(2)
C51	C14	N3	120.2(2)	C43	C41	C40	112.0(2)
C51	C14	C13	119.8(2)	C43	C41	C42	109.3(2)
C16	C15	N3	120.3(2)	C43	C41	C49	108.5(2)
C27	C15	N3	119.7(2)	C44	C43	C41	122.4(2)
C27	C15	C16	120.0(2)	C48	C43	C41	119.7(2)
C15	C16	C20	122.1(2)	C48	C43	C44	118.0(2)
C17	C16	C15	117.5(2)	C43	C44	N1	120.7(2)
C17	C16	C20	120.2(2)	C45	C44	N1	120.1(2)

C18	C17	C16	122.6(2)	C45	C44	C43	119.3(2)
C28	C18	C17	119.2(2)	C46	C45	C44	120.6(3)
C16	C20	C19	108.5(2)	C47	C46	C45	120.6(3)
C16	C20	C21	110.49(19)	C48	C47	C46	118.7(3)
C16	C20	C52	110.4(2)	C47	C48	C43	122.9(3)
C19	C20	C52	108.6(2)	C51	C50	C11	120.1(2)
C21	C20	C19	109.5(2)	C14	C51	C50	120.3(2)

8. NMR Spectra

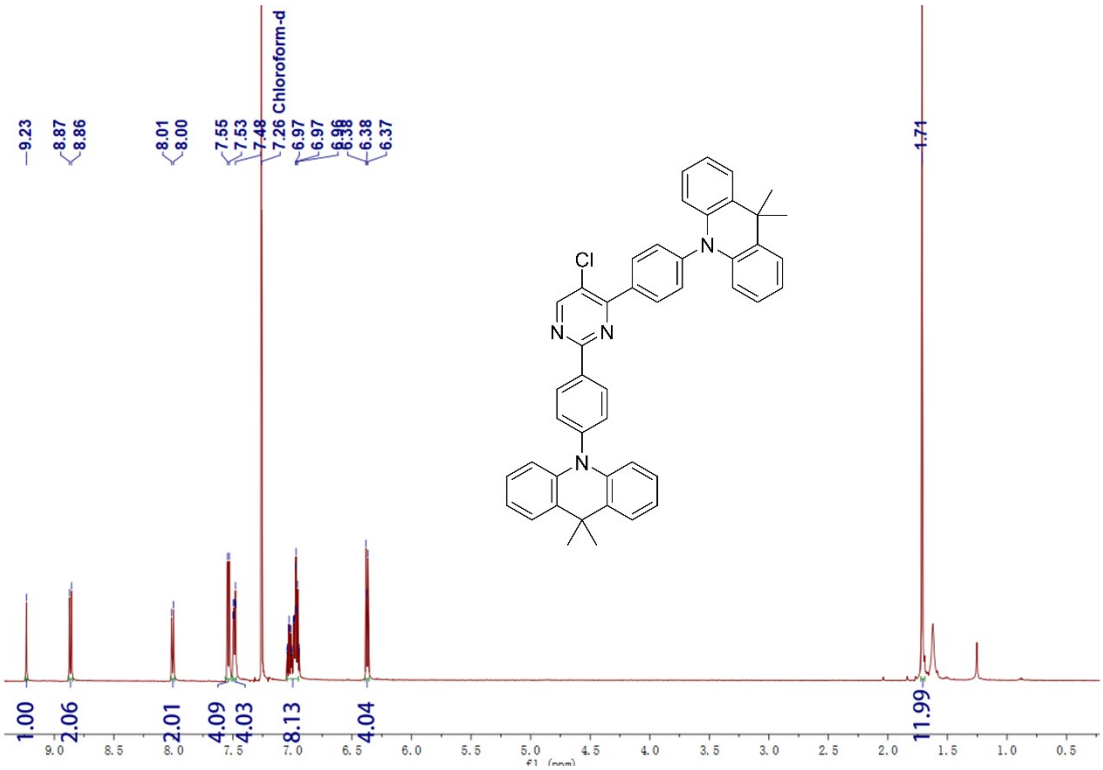


Figure S11. ^{1}H-NMR spectrum of Cl-Pym-DMAC (500 MHz, $CDCl_3$).

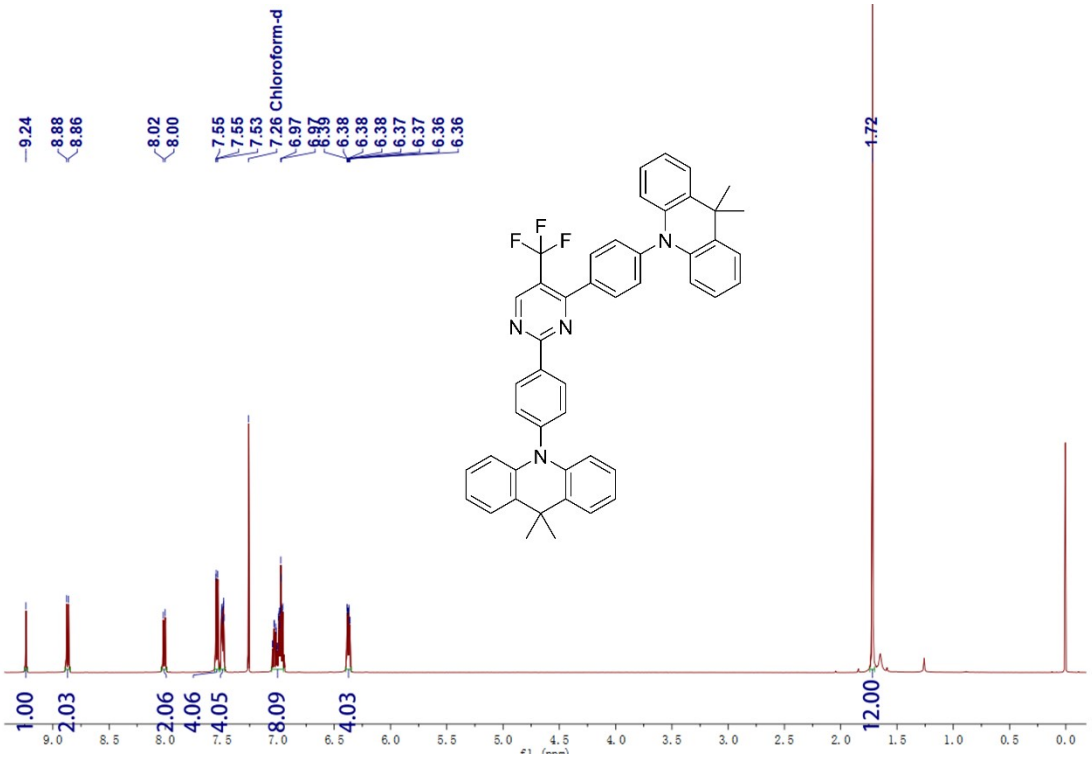


Figure S12. ^{1}H-NMR spectrum of CF_3-Pym-DMAC (500 MHz, $CDCl_3$).

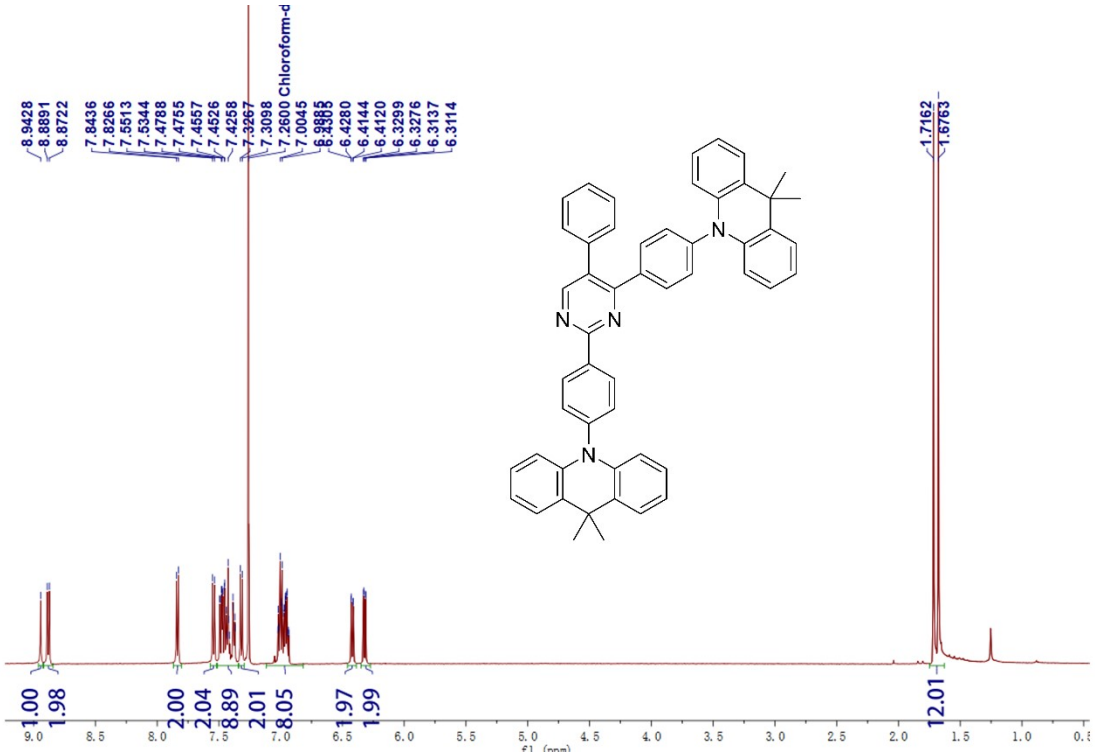


Figure S13. ^{1}H-NMR spectrum of Ph-Pym-DMAC (500 MHz, $CDCl_3$).

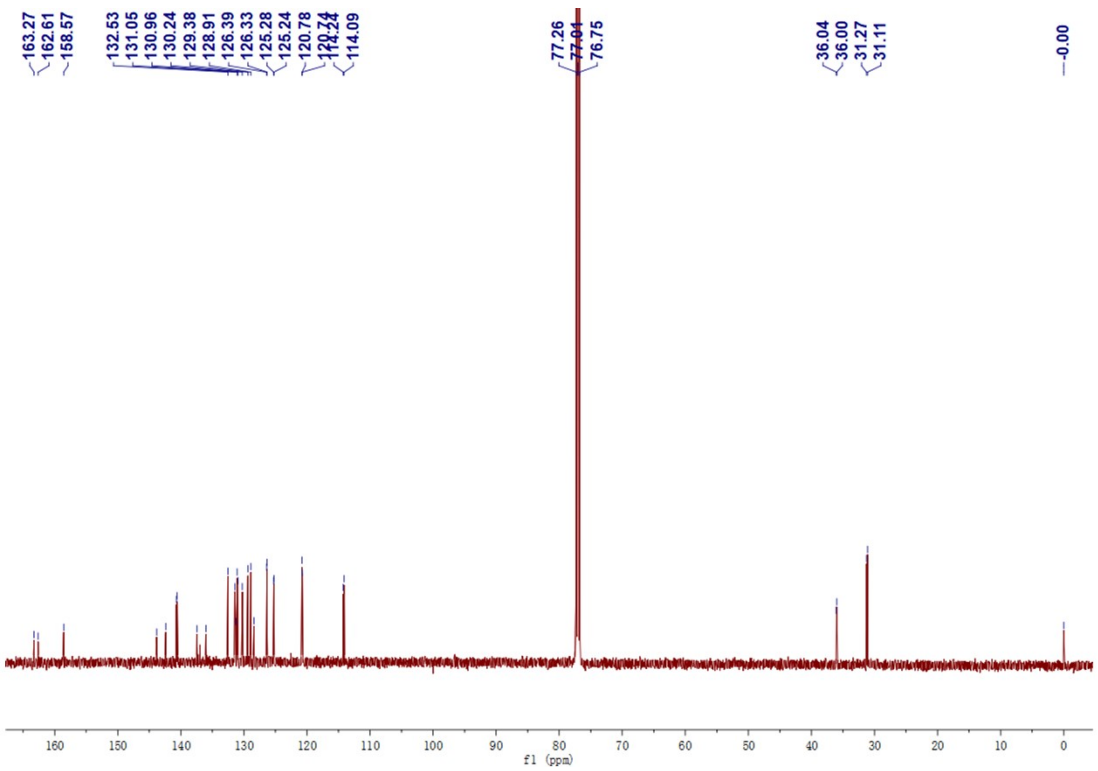


Figure S14. ^{13}C-NMR spectrum of Ph-Pym-DMAC (126 MHz, $CDCl_3$).

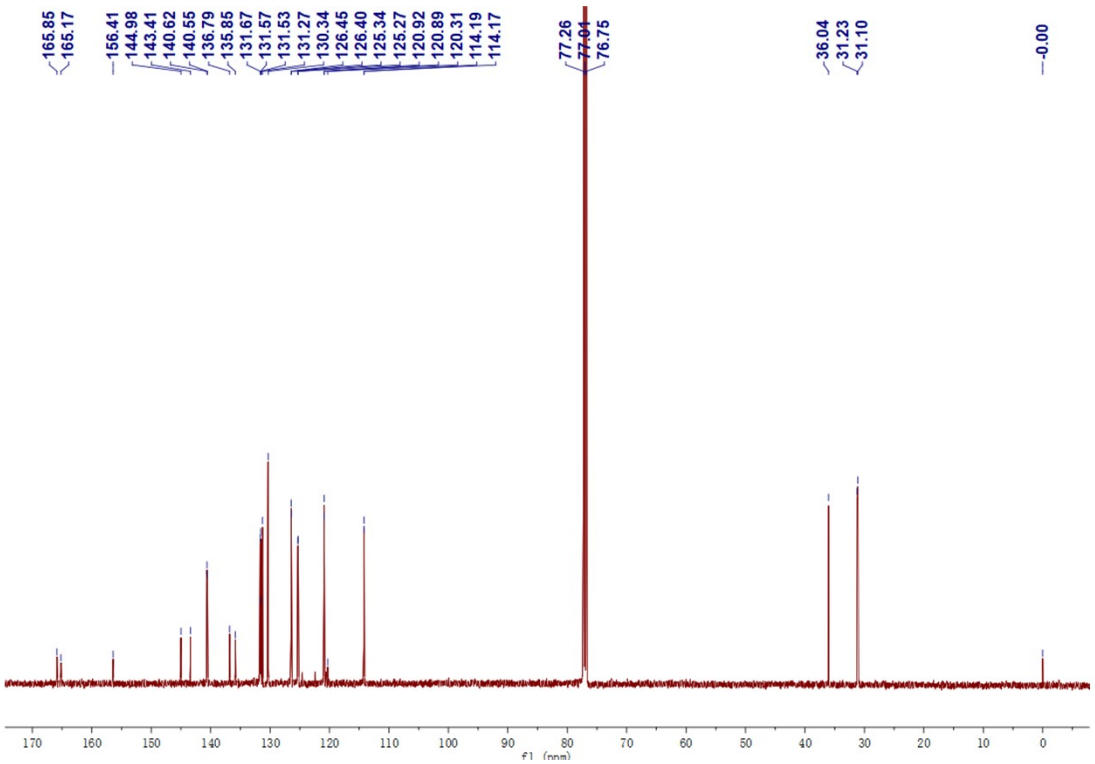


Figure S15. ^{13}C-NMR spectrum of CF_3-Pym-DMAC (126 MHz, $CDCl_3$).

9. Mass Spectra

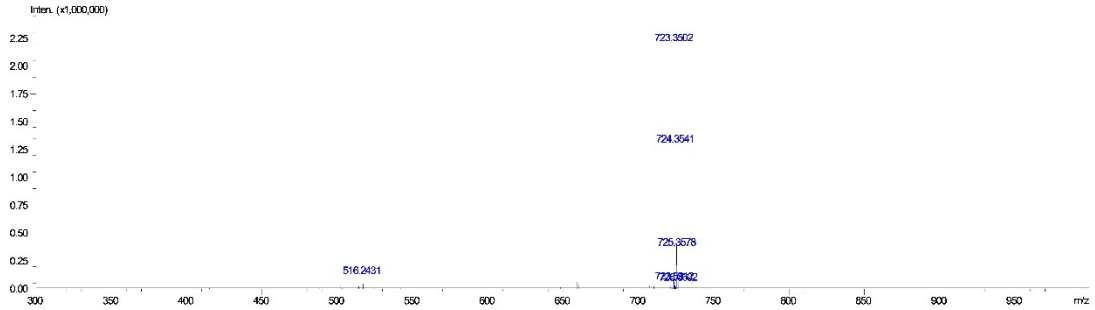


Figure S16. Mass spectrum of Ph-Pym-DMAC.

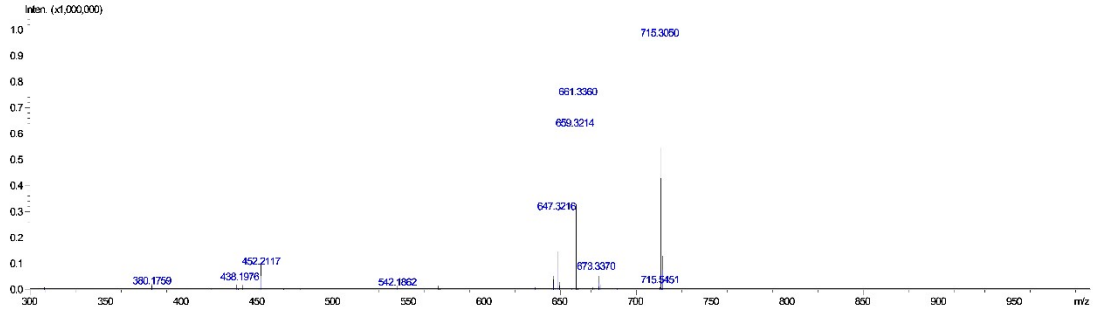


Figure S17. Mass spectrum of CF_3-Pym-DMAC.

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