

Supplementary Materials

Efficient Exciplex-Based Deep-Blue Organic Light-Emitting Diodes Employing a Bis(4-fluorophenyl) amine-Substituted Heptazine Acceptor

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1. Instrumentation

NMR spectra were obtained on a Varian Inova 400 spectrometer. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) chemical shifts were measured relative to DMSO- d_6 as the internal reference (DMSO- d_6 : $\delta = 2.50$ ppm for ^1H and $\delta = 39.52$ ppm for ^{13}C respectively). High-resolution mass spectra (HRMS) were obtained with Waters-Q-TOF-Premier (ESI $^+$). The UV and PL spectra were recorded with a Shimadzu UV-2550 spectrophotometer and Shimadzu RF-5301PC fluorescence spectrometer, respectively. The PLQY and transient PL decay were recorded using a Hamamatsu C9920-02 and a Hamamatsu C11367-03 measurement system, respectively. Transient PL decay characteristics of film samples under vacuum conditions were measured on a streak camera (C4334, Hamamatsu Photonics) equipped with cryostat using a YAG laser. The highest occupied molecular orbital (HOMO) energy levels of HAP-3FDPA and mCP were determined by atmospheric ultraviolet photoelectron spectroscopy (AC-3E, Riken Keiki), and the corresponding lowest unoccupied molecular orbital (LUMO) levels were calculated by subtracting the energy gaps from the HOMO levels. Oxygen-free sample solutions (1×10^{-4} mol L $^{-1}$) were degassed with N $_2$ for 15 min prior to use unless otherwise indicated. Pure and doped films were deposited on quartz and silicon substrates by vacuum thermal evaporation at a pressure lower than 5×10^{-4} Pa.

2. Quantum Chemical Calculations

All calculations were performed using the Gaussian 09 program package. The HOMO and LUMO of HAP-3FDPA were calculated using the nonlocal density functional of Becke's 3-parameters employing Lee-Yang-Parr functional (B3LYP) with the 6-31G(d) basis set. Their S_1 and T_1 were calculated by the time-dependent density functional theory (TD-DFT) method at the optimized ground-state geometries using the B3LYP mode with a 6-31G(d) basis set [S1].

2.1 The Optimized Geometry Data for HAP-3FDPA (unit: Å)

C	-7.01210465	-1.70088527	-0.09624241
C	-6.54392461	-2.42884946	0.99099161
C	-5.18769035	-2.74392982	1.05169564
C	-4.31985395	-2.33820662	0.03287356
C	-4.81732526	-1.61455175	-1.05631107
C	-6.16925764	-1.28681791	-1.12185208
N	-2.93472063	-2.72478931	0.09912647
C	-1.92679378	-1.79004971	0.06266245
N	-2.30715943	-0.49936494	0.06483414
C	-1.34478238	0.41434050	0.02839837
N	0.00081352	-0.00108659	-0.00452858
C	0.31406057	-1.37413160	-0.00100236

N	-0.66886392	-2.26584232	0.02838510
N	-1.62512233	1.71193362	0.02946096
C	-0.58385735	2.56328517	-0.00495091
N	0.72343172	2.24719198	-0.04221759
C	1.03337410	0.95637302	-0.04056061
N	2.29677222	0.55019137	-0.07752022
C	2.51368560	-0.77765666	-0.06913366
N	1.58637309	-1.75152253	-0.02736657
N	-0.88960003	3.90391712	0.00001975
N	3.82691654	-1.18377219	-0.10528852
C	4.18567442	-2.57485716	-0.19601790
C	-2.25125892	4.36642864	-0.06201825
C	0.13570589	4.91146572	0.07147079
C	0.17934428	5.90659226	-0.91033295
C	1.12686065	6.92631973	-0.84109708
C	2.02792346	6.92975838	0.21672683
C	2.00453309	5.95186607	1.20515365
C	1.04784761	4.94250341	1.13213814
C	5.06032418	-3.11228057	0.75410718
C	5.46674172	-4.44259541	0.66802628
C	4.98153466	-5.22290662	-0.37438456
C	4.11195608	-4.71167451	-1.33153914
C	3.71947132	-3.37843805	-1.24258944
C	-2.72146608	5.22751784	0.93470183
C	-4.01875562	5.73336662	0.87659541
C	-4.83381111	5.36056633	-0.18536947
C	-4.38922116	4.50651090	-1.18870822
C	-3.08817211	4.01361846	-1.12642164
C	-2.65736913	-4.13314665	0.20473396
C	-1.88947322	-4.64537068	1.25672480
C	-1.66707844	-6.01622747	1.36004503
C	-2.23044581	-6.86330705	0.41207618
C	-3.00539187	-6.38035978	-0.63537029
C	-3.21385017	-5.00603874	-0.73602622
F	-8.32315558	-1.39068935	-0.16174329
F	-2.02204708	-8.19209959	0.51488909
F	-6.09129465	5.84454633	-0.24751864
F	5.36837973	-6.51215519	-0.46302700
F	2.94908957	7.91236184	0.28992221
C	4.90919046	-0.23596968	-0.05527479
C	5.86730127	-0.24648730	-1.07405501
C	6.95483868	0.62383891	-1.02984155
C	7.06304638	1.50315745	0.04075836
C	6.12371903	1.53255441	1.06570800
C	5.04551476	0.65238141	1.01704185

F	8.11195924	2.34974584	0.09027066
H	-7.23240564	-2.73364195	1.77192129
H	-4.79930230	-3.31137400	1.89137647
H	-4.14295479	-1.29705541	-1.84307353
H	-6.57473701	-0.72186797	-1.95444495
H	-0.53395358	5.88351415	-1.72798066
H	1.17654925	7.70587354	-1.59383376
H	2.72408632	5.99140662	2.01601183
H	1.01704570	4.16893257	1.89046405
H	5.42705649	-2.48482274	1.56014245
H	6.14390603	-4.87656476	1.39600747
H	3.75599282	-5.35283854	-2.13089287
H	3.03726748	-2.96480002	-1.97573888
H	-2.06734996	5.50472066	1.75517260
H	-4.40150230	6.40140199	1.64080597
H	-5.05617951	4.24114400	-2.00207410
H	-2.72484995	3.34235076	-1.89576933
H	-1.45296575	-3.97024444	1.98308750
H	-1.06904595	-6.43199335	2.16395656
H	-3.42867850	-7.07191512	-1.35608463
H	-3.81575089	-4.60759734	-1.54642550
H	5.76216767	-0.94167051	-1.90084521
H	7.70741250	0.63111340	-1.81109406
H	6.24540180	2.23291318	1.88515984
H	4.29993582	0.66339222	1.80349778

2.2 Excitation Energies and Oscillator Strengths for HAP-3FDPA

Excited State 1: Triplet-A 3.2734 eV 378.77 nm f=0.0000

198 → 202	0.11849
198 → 203	0.10932
199 → 201	0.42667
199 → 203	-0.11350
200 → 201	0.45364
200 → 202	-0.12793

Excited State 2: Triplet-A 3.2746 eV 378.62 nm f=0.0000

198 → 202	0.10563
198 → 203	-0.12371
199 → 201	0.45332
199 → 202	0.13109
200 → 201	-0.42716
200 → 203	-0.10262

Excited State 3: Triplet-A 3.3514 eV 369.95 nm f=0.0000

198 → 201	0.57236
199 → 202	0.21785

200 → 203	0.23633				
200 → 213	0.10649				
Excited State 4: Triplet-A	3.5277 eV	351.46 nm	f=0.0000		
197 → 201	0.55171				
198 → 208	-0.15420				
199 → 203	-0.14323				
199 → 209	0.16301				
200 → 202	0.14113				
200 → 207	0.15575				
Excited State 5: Singlet-A	3.5639 eV	347.89 nm	f=0.0000		
197 → 201	0.67884				
Excited State 6: Singlet-A	3.6477 eV	339.89 nm	f=0.3930		
200 → 201	0.67448				
Excited State 7: Singlet-A	3.6811 eV	336.81 nm	f=0.4048		
199 → 201	0.67851				
Excited State 8: Singlet-A	3.6876 eV	336.22 nm	f=0.0009		
198 → 201	0.64391				

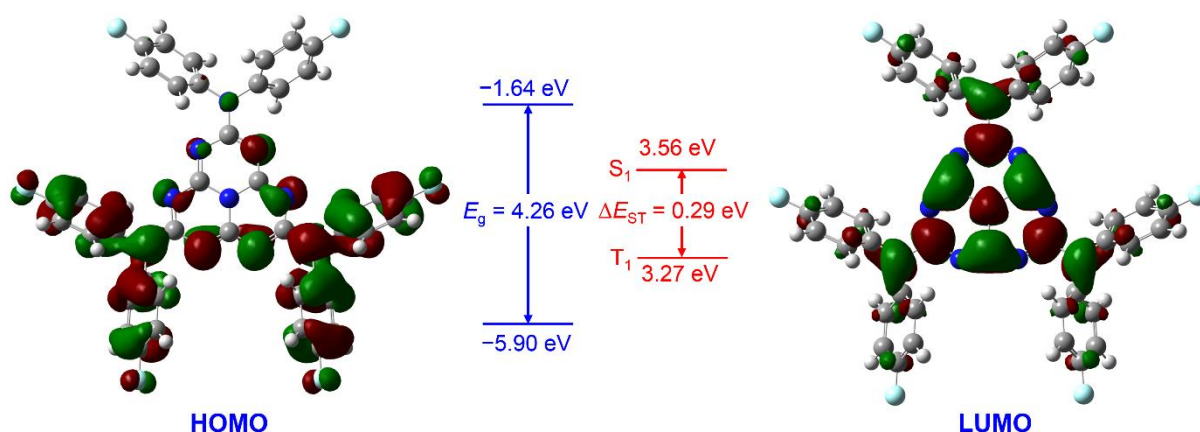


Figure S1. Frontier molecular orbital distributions and energy levels of the lowest excited singlet and triplet states of HAP-3FDPA by theoretical calculations.

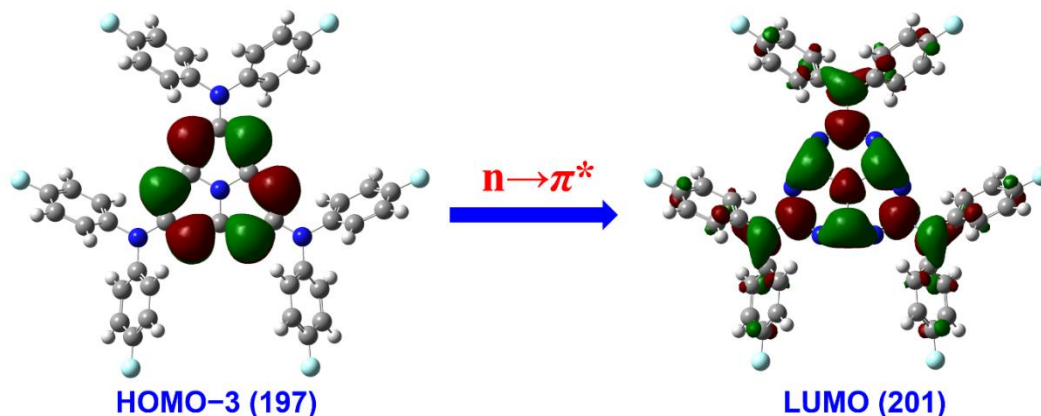


Figure S2. The natural transition orbitals (197 → 201) for the lowest excited singlet state (S_1) of HAP-3FDPA by theoretical calculations.

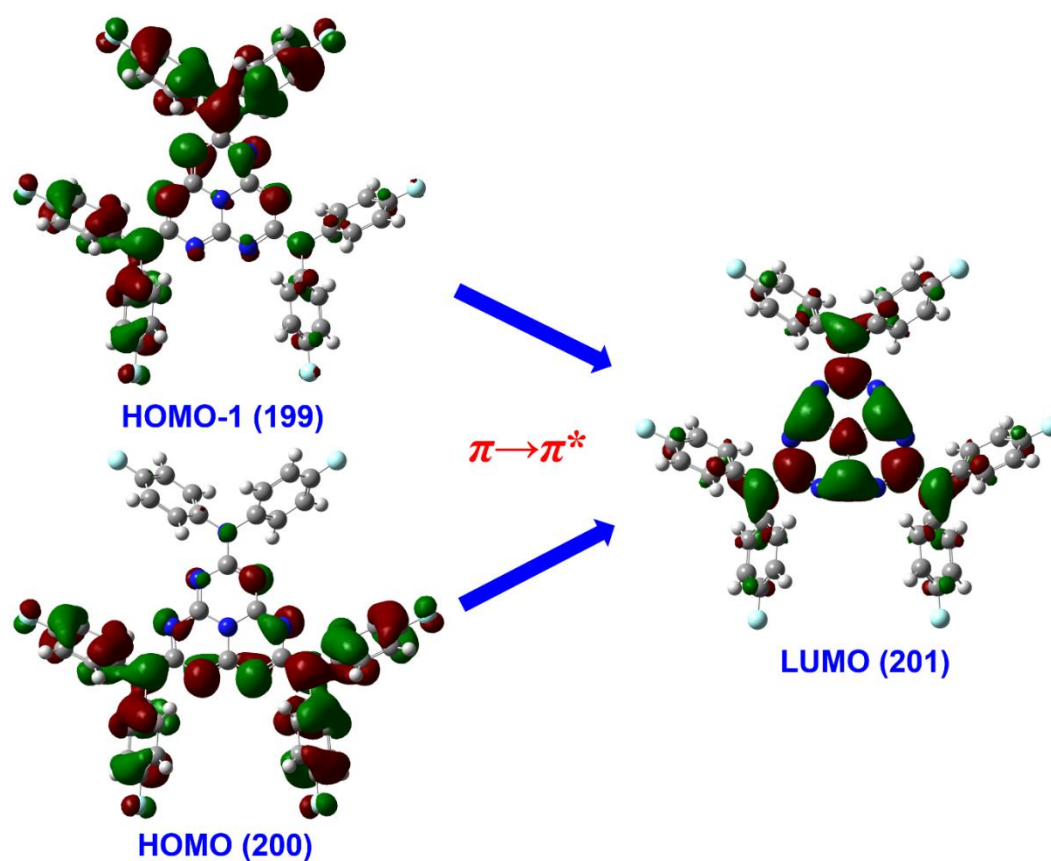


Figure S3. The natural transition orbitals (199 \rightarrow 201) and (200 \rightarrow 201) for the lowest excited triplet state (T_1) of HAP-3FDPA by theoretical calculations.

3. Photophysical Properties

Table S1. The PLQYs of HAP-3FDPA:mCP doped films at various concentrations.

Concentration	PLQY
8 wt% HAP-3FDPA:mCP	53.2%
25 wt% HAP-3FDPA:mCP	41.6%
50 wt% HAP-3FDPA:mCP	37.1%
100 wt% HAP-3FDPA:mCP	5.1%

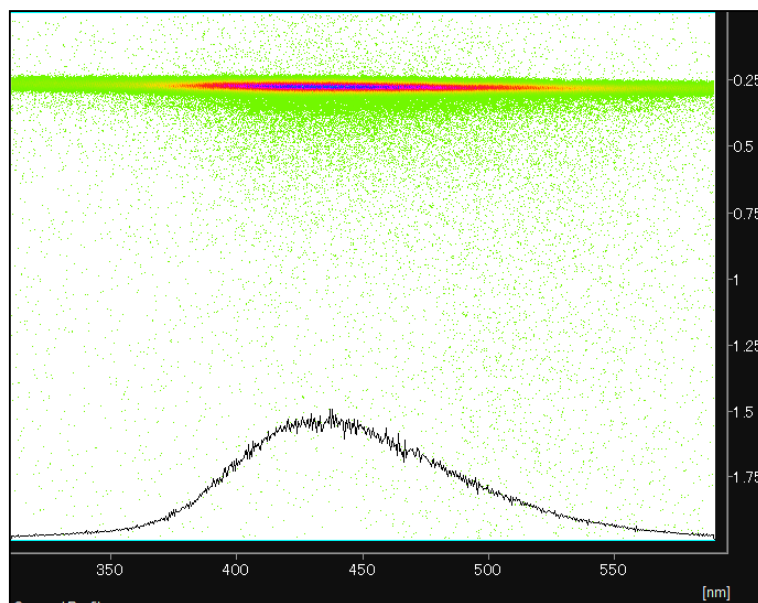


Figure S4. The transient PL decay image of 8 wt% HAP-3FDPA:mCP doped film in the time range of 2 μ s.

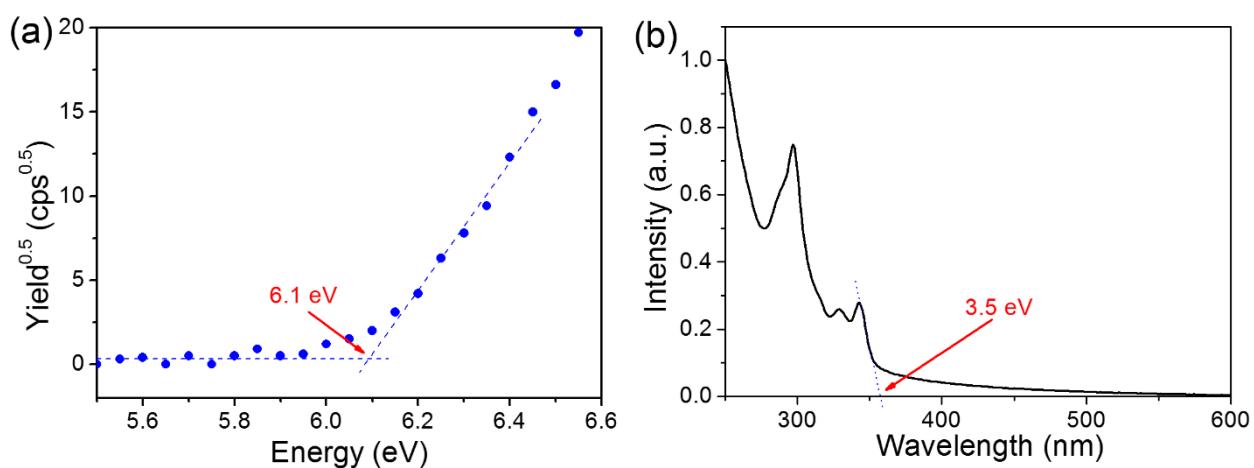


Figure S5. (a) The HOMO energy level of mCP determined by atmospheric ultraviolet photoelectron spectroscopy. (b) The UV spectra of mCP in a neat film. The optical energy gap of mCP was calculated to be 3.5 eV. Therefore, the LUMO energy level of mCP could be calculated to be -2.6 eV.

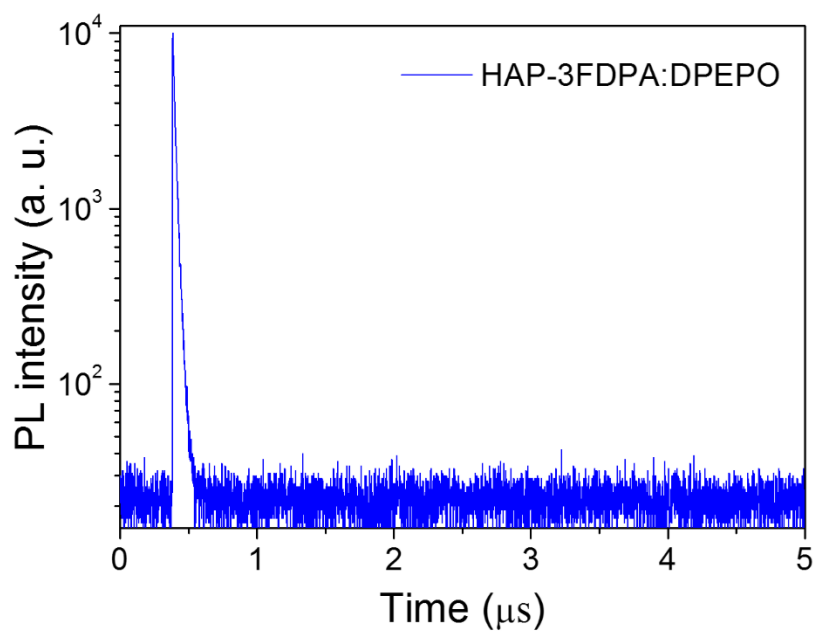


Figure S6. The transient PL decay of 8 wt% HAP-3FDPA:DPEPO doped film in the time range of 5 μ s.

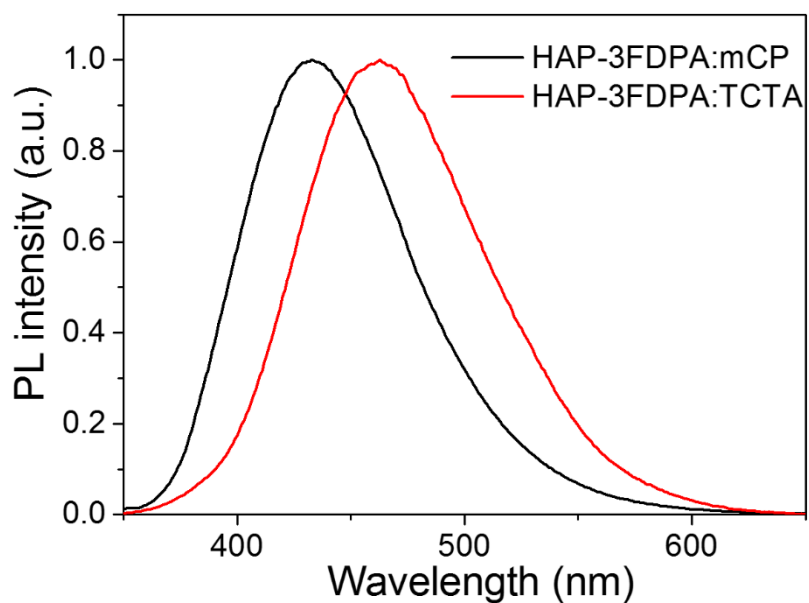


Figure S7. The PL spectrum of 8 wt% HAP-3FDPA:TCTA doped film as compared to that of 8 wt% HAP-3FDPA:mCP.

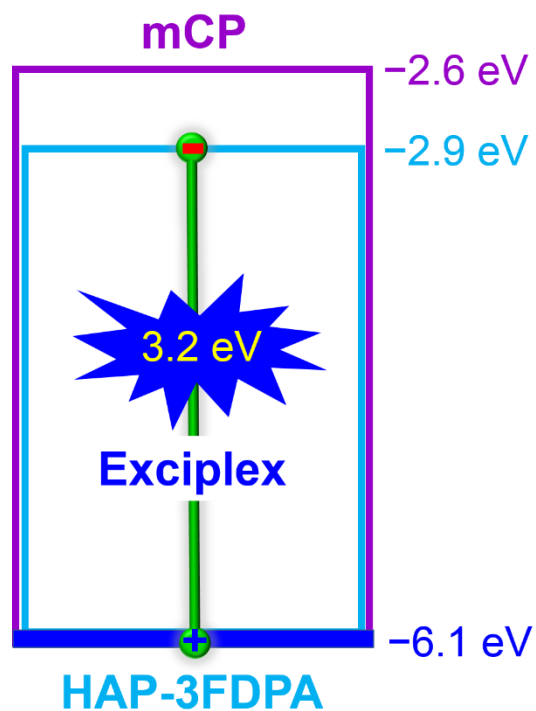


Figure S8. The energy diagram of the 8 wt% HAP-3FDPA:mCP exciplex system.

4. ^1H and ^{13}C NMR spectra of HAP-3FDPA

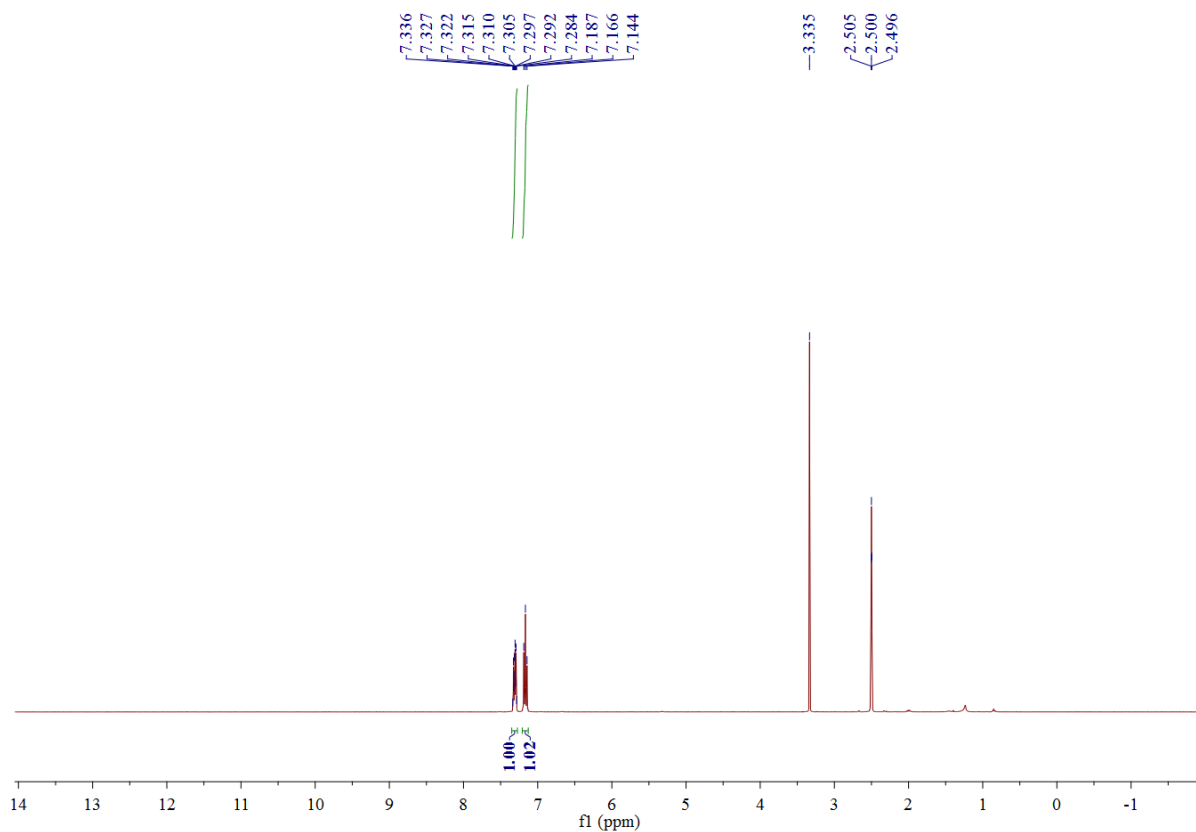


Figure S9. ^1H NMR spectrum of HAP-3FDPA in $\text{DMSO-}d_6$.

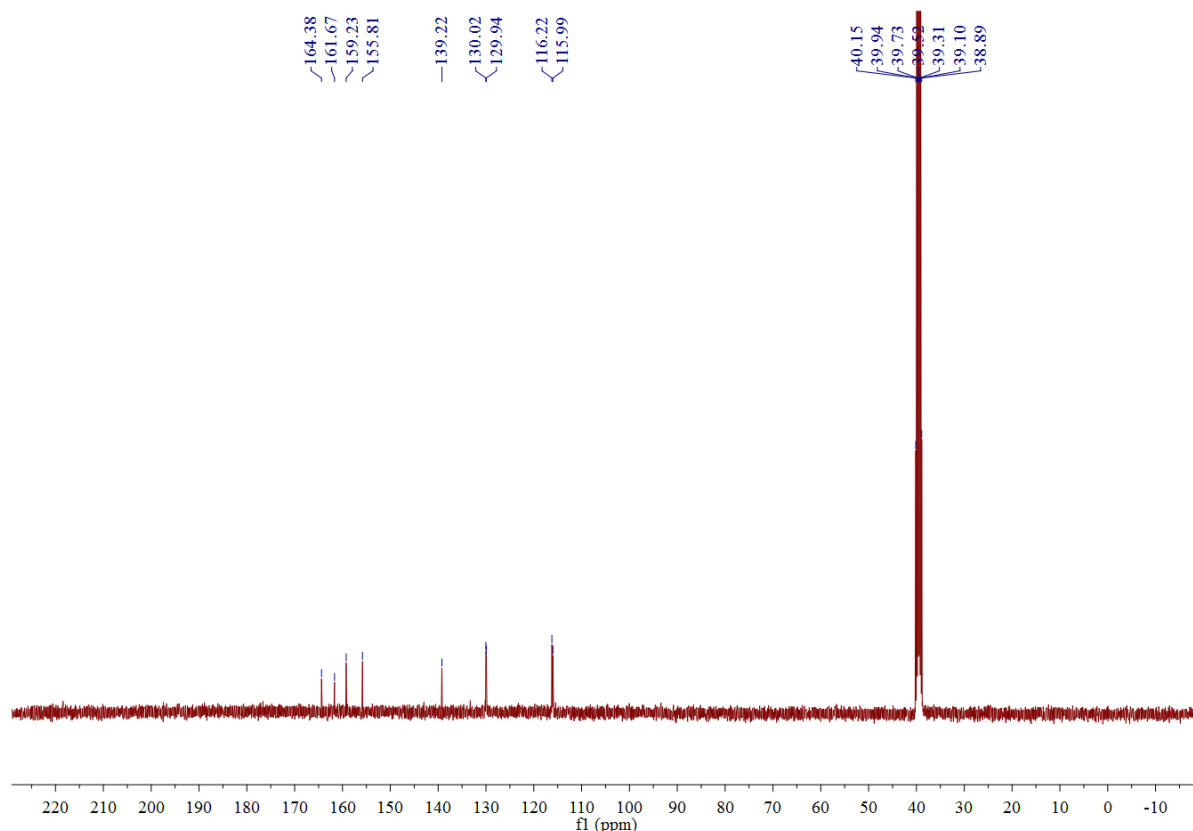


Figure S10. ^{13}C NMR spectrum of HAP-3FDPA in $\text{DMSO-}d_6$.

5. References

- S1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision C.01*. (Gaussian, Inc., 2009).