Supporting Information

Experimental and Computational Studies on the Effects of C(2) Methylation on the Properties and Gas Separation Performance of Polyimide-Ionene Membranes

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^{1}H- and ^{13}C-NMR: Monomers and Ionenes

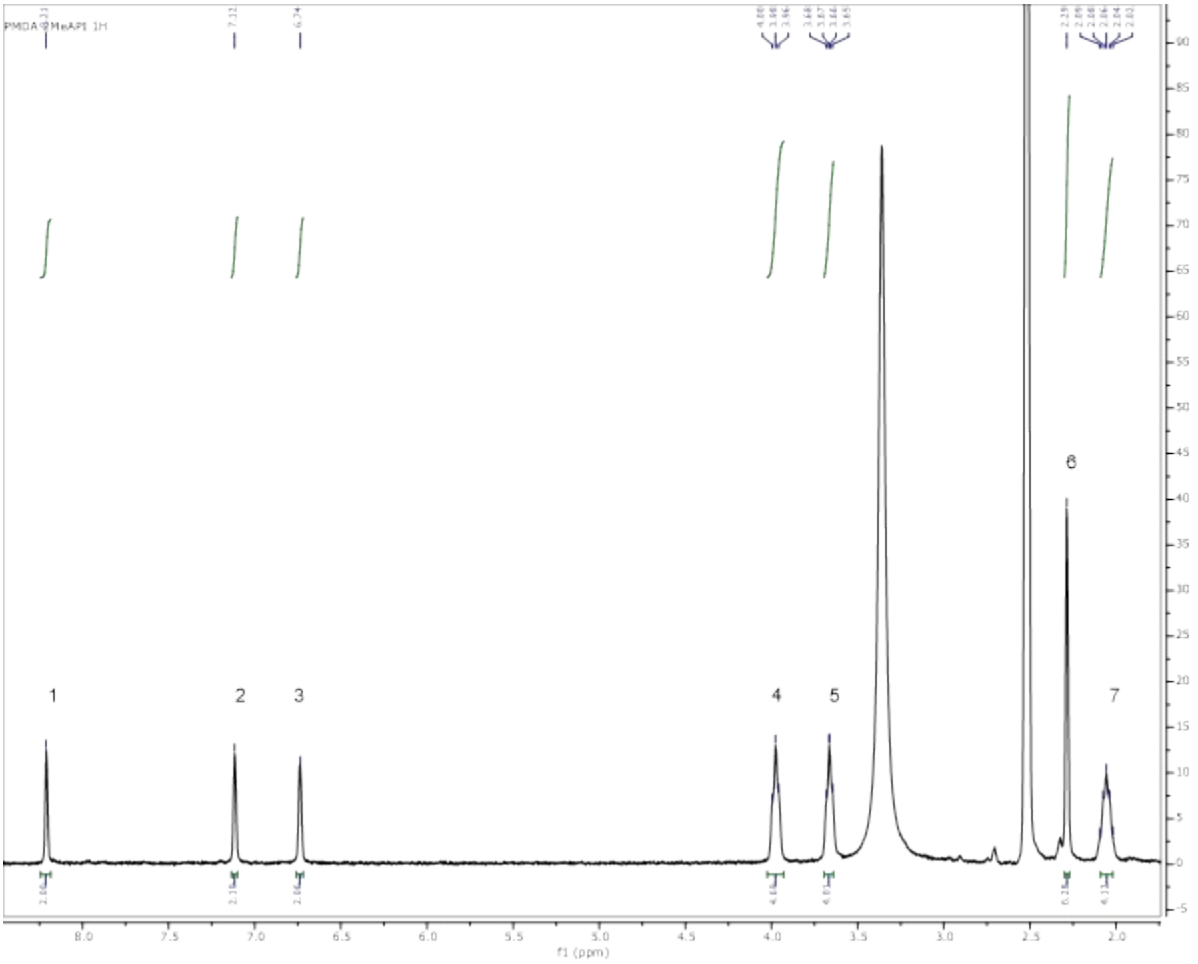
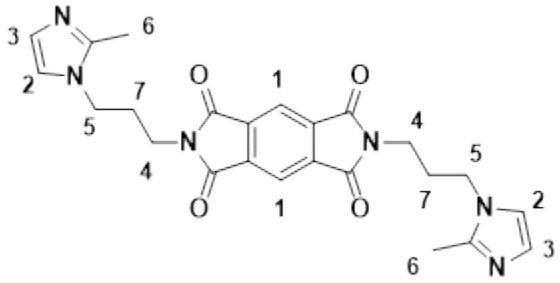


Figure S1. ^{1}H-NMR spectrum for PMDA 2MeAPI.



^{1}H-NMR (500MHz, d6-DMSO) δ 8.21 (s, 2H), 7.12 (s, 2H), 6.74 (s, 2H), 3.98 (t, J = 7.24 Hz, 4H), 3.66 (t, J = 6.10 Hz, 4H), 2.29 (s, 6H), 2.06 (p, J = 6.51, 6.71 Hz, 4H).

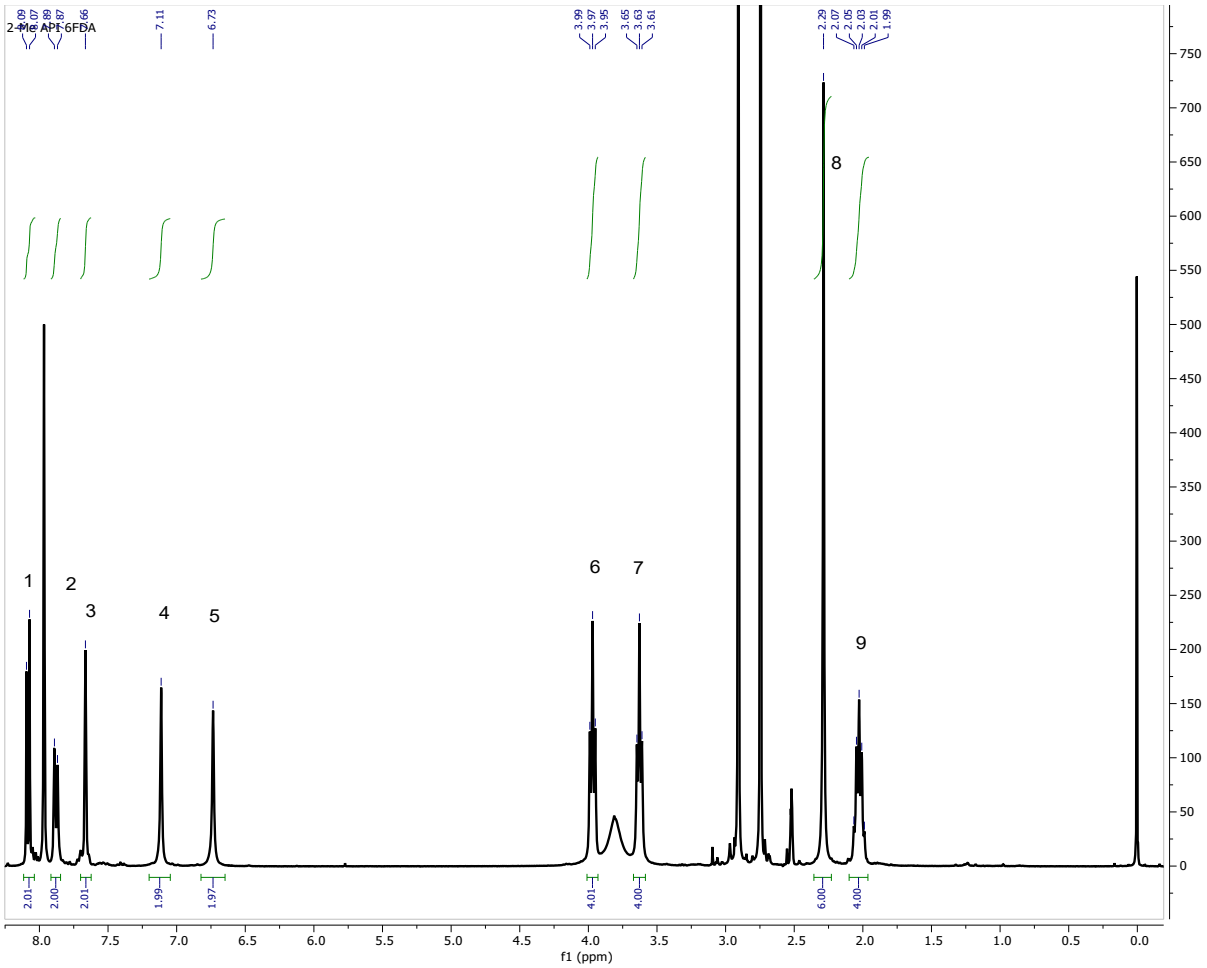
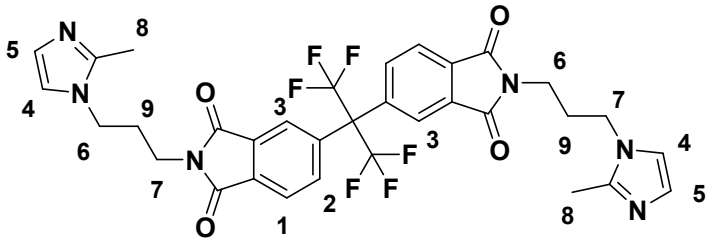


Figure S2. ^{1}H-NMR spectrum for 6FDA 2MeAPI.



^{1}H-NMR (500MHz, d6-DMSO) δ 8.08 (d, J = 8.06 Hz, 2H), 7.88 (d, J = 7.99 Hz, 2H), 7.66 (s, 2H), 7.11(s, 2H), 6.73 (s, 2H), 3.97 (t, J = 7.11 Hz, 4H), 3.63 (t, J = 6.62 Hz, 4H), 2.29 (s, 6H), 2.03 (p, J = 6.76, 6.93 Hz, 4H). Some residual toluene is evident.

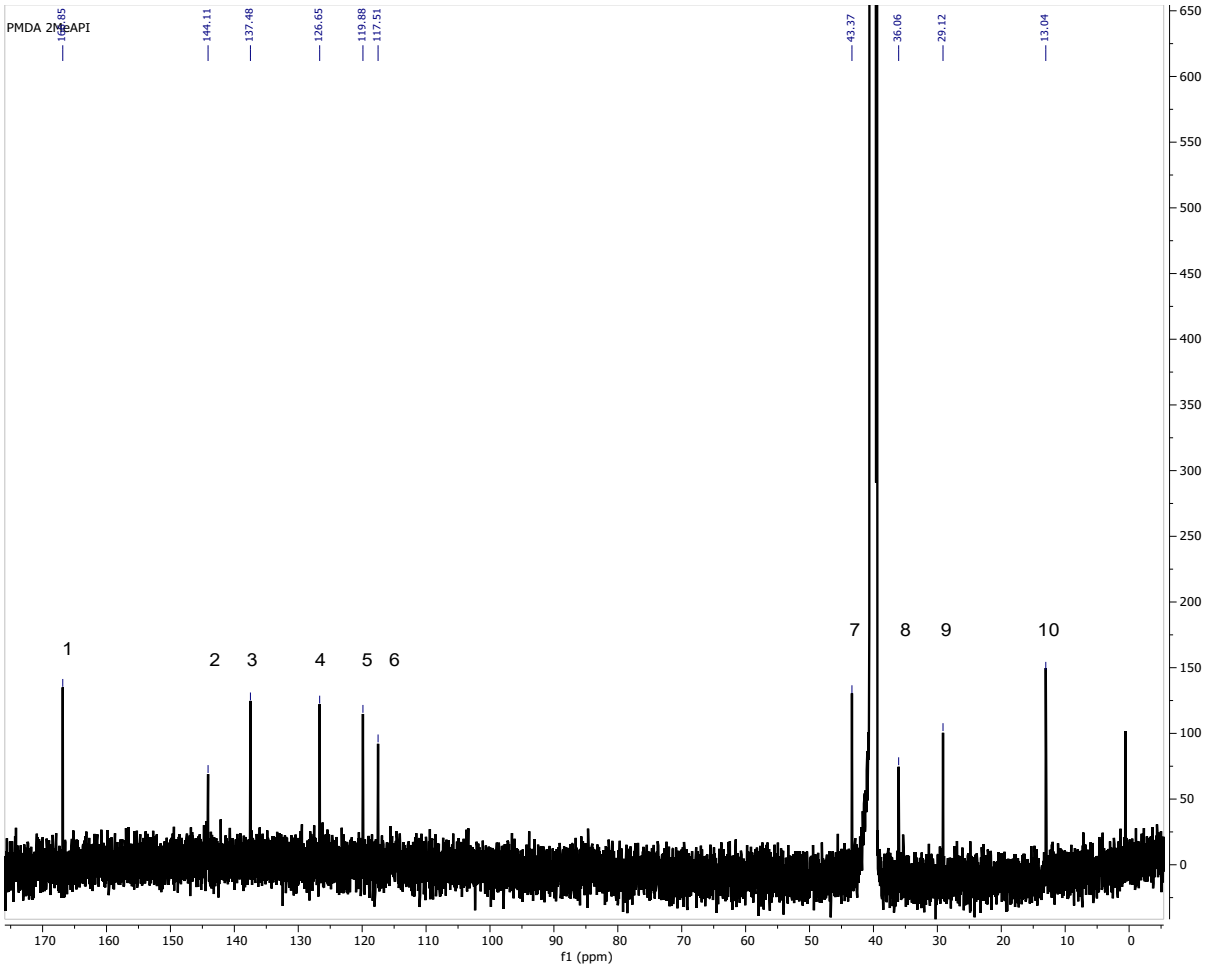
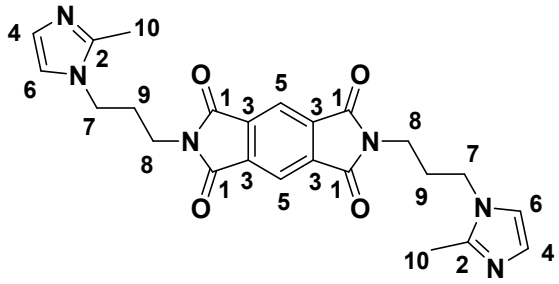


Figure S3. ^{13}C-NMR spectrum for PMDA 2MeAPI.



^{13}C-NMR (500MHz, d6-DMSO) δ 166.85 (C-1, 4C), 144.11 (C-2,2C), 137.48 (C-3,4C), 126.65 (C-4,2C), 119.88 (C-5,2C), 117.51 (C-6,2C), 43.37 (C-7,2C), 36.06 (C-8, 2C), 29.12 (C-9, 2C), 13.04 (C-10, 2C).

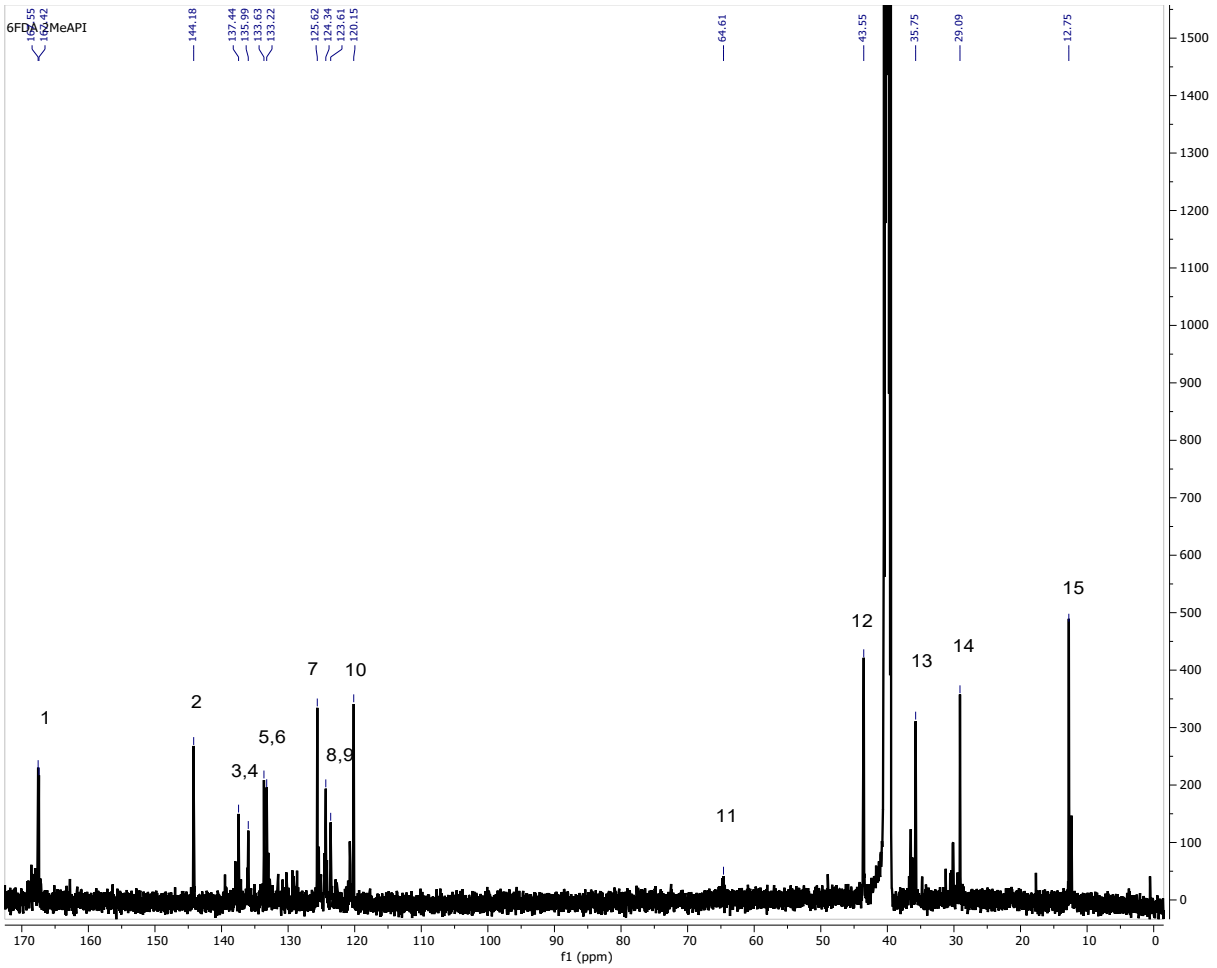
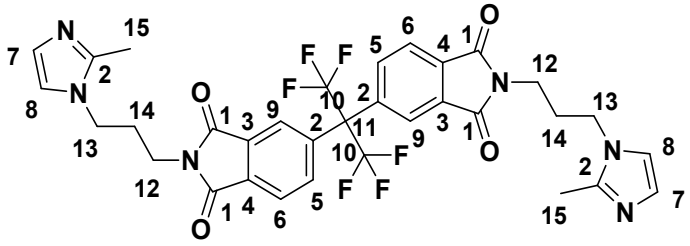


Figure S4. ^{13}C-NMR spectrum for 6FDA 2MeAPI.



^{13}C-NMR (500MHz, d6-DMSO) δ167.55, 167.42, 144.18, 137.44, 135.99, 133.63, 133.22, 125.62, 124.34, 123.61, 120.15, 64.61, 43.55, 35.75, 29.09,12.75.

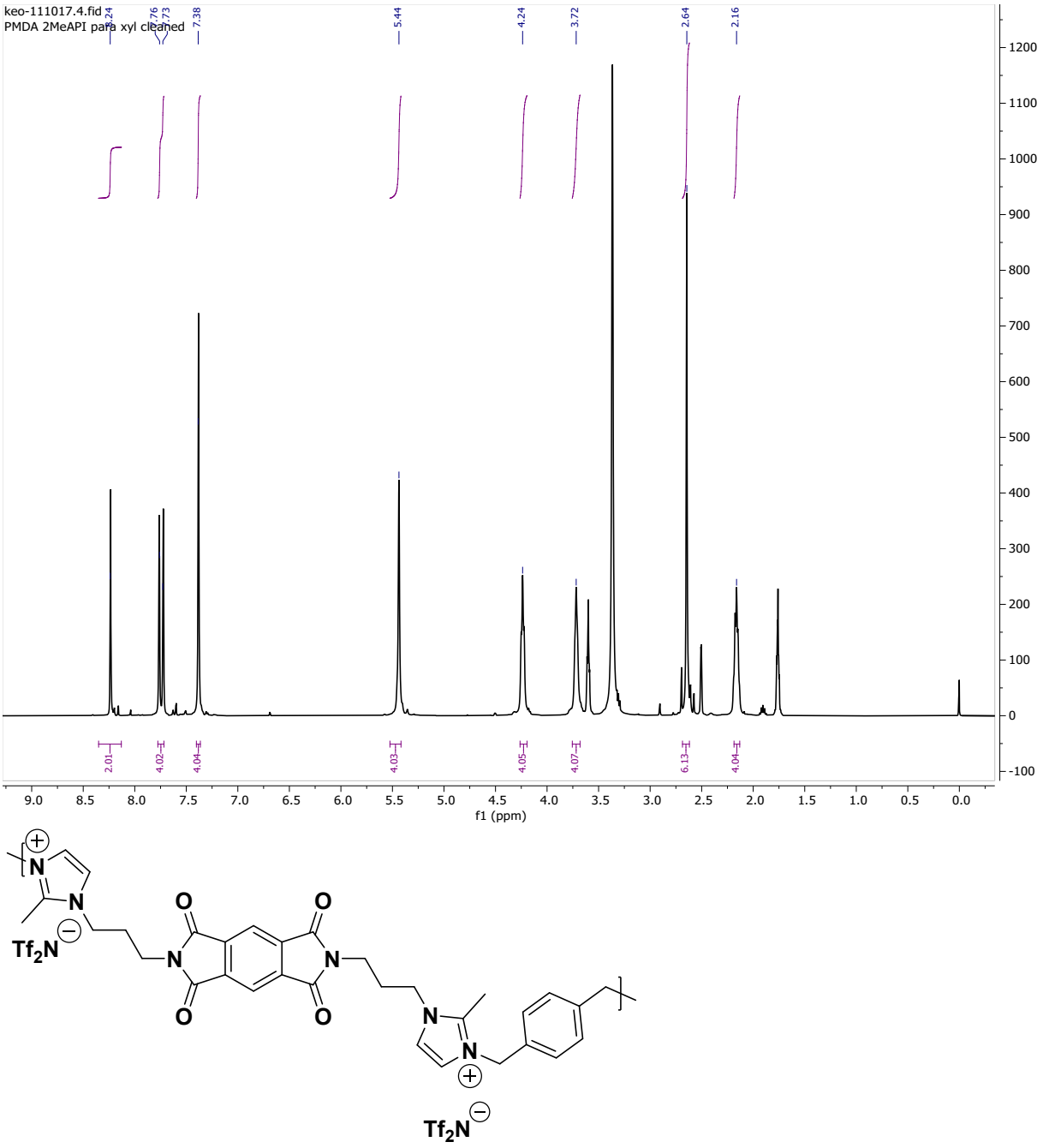


Figure S5: ^{1}H-NMR for [PMDA-2MeAPI(pXy)][Tf_2N].

^{1}H NMR (500 MHz, DMSO) δ 8.24 (s, 2H), 7.74 (d, J = 15.8 Hz, 4H), 7.38 (s, 4H), 5.44 (s, 4H), 4.24 (s, 4H), 3.72 (s, 4H), 2.64 (s, 6H), 2.16 (s, 4H). Some residual NMP is present.

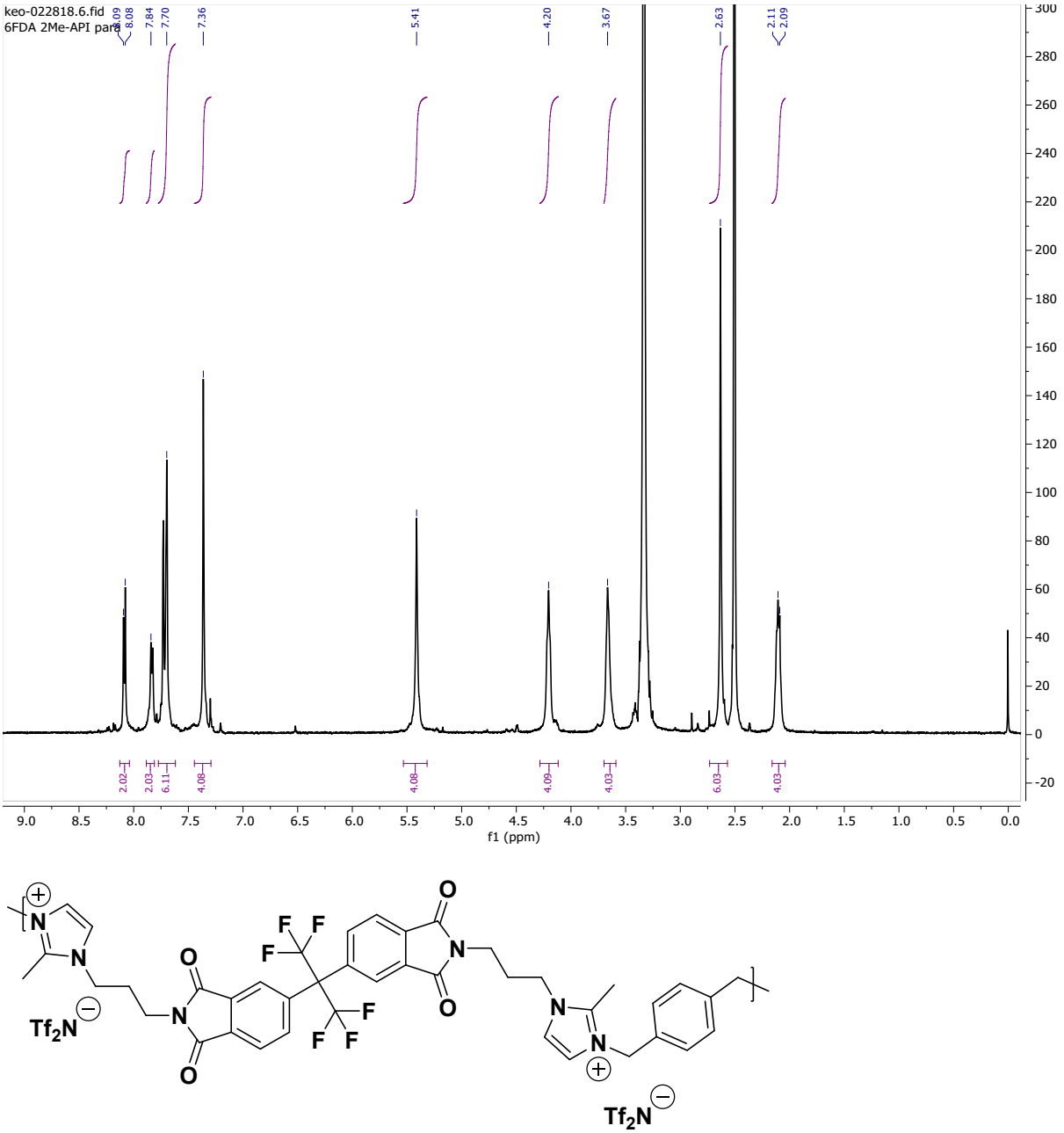


Figure S6: ^{1}H-NMR for [6FDA-2MeAPI(pXy)][Tf_2N].

^{1}H NMR (500 MHz, DMSO) δ 8.09 (d, J = 8.1 Hz, 2H), 7.84 (s, 2H), 7.70 (s, 6H), 7.36 (s, 4H), 5.41 (s, 4H), 4.20 (s, 4H), 3.67 (s, 4H), 2.63 (s, 6H), 2.10 (d, J = 8.0 Hz, 4H).

FT-IR Analysis

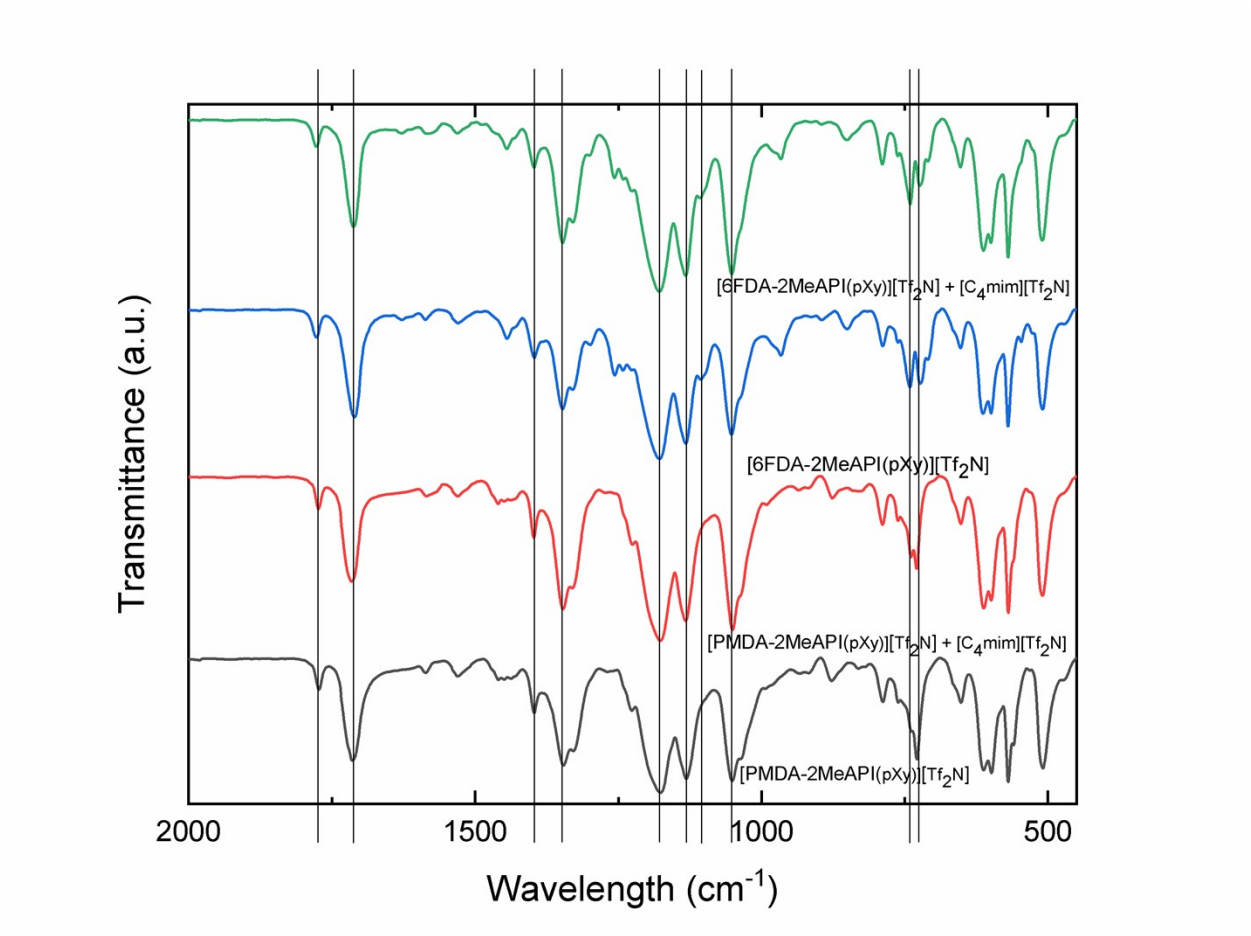


Figure S7. FT-IR spectra of all neat and composite materials with main groups indicated.

MALDI-TOF MS

The number average molecular weights (M_N) for both [PMDA-2MeAPI(pXy)][Tf_2N] and [6FDA-2MeAPI(pXy)][Tf_2N] ionenes were determined using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). MALDI-TOF MS charcterizations were conducted in the linear mode using a Bruker Rapiflex instrument, optimized for MW ranges between 20-250 kDa and using THAP in MeOH as the matrix.

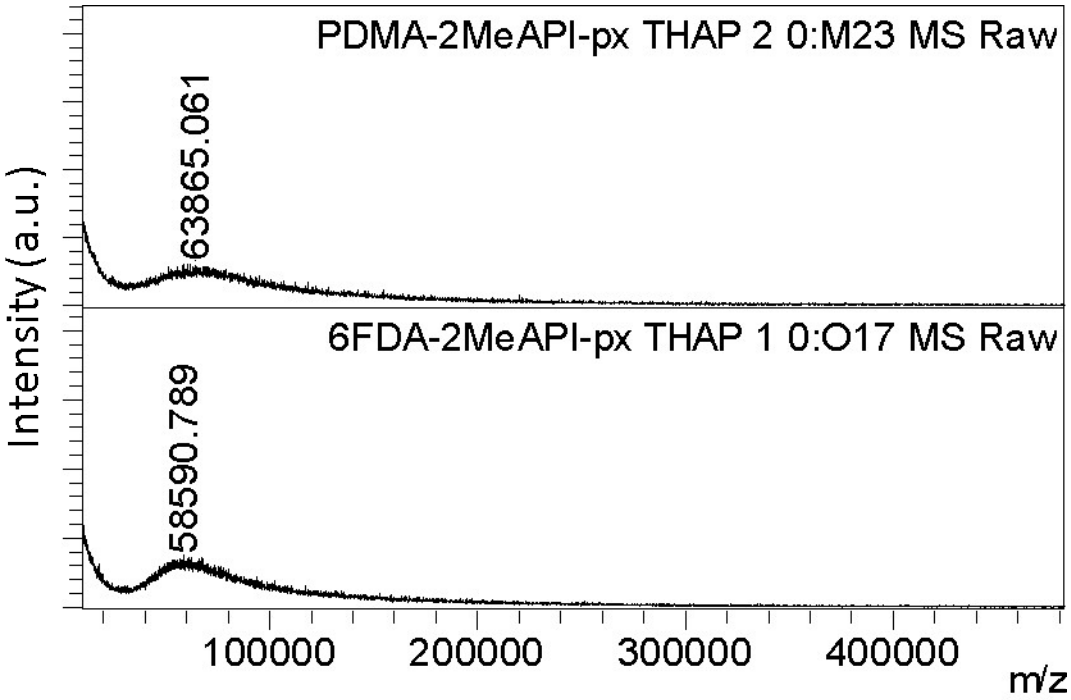


Figure S8. MALDI-TOF profile for newly synthesized ionenes, labeled with value of M_N (amu).

Thermal Data

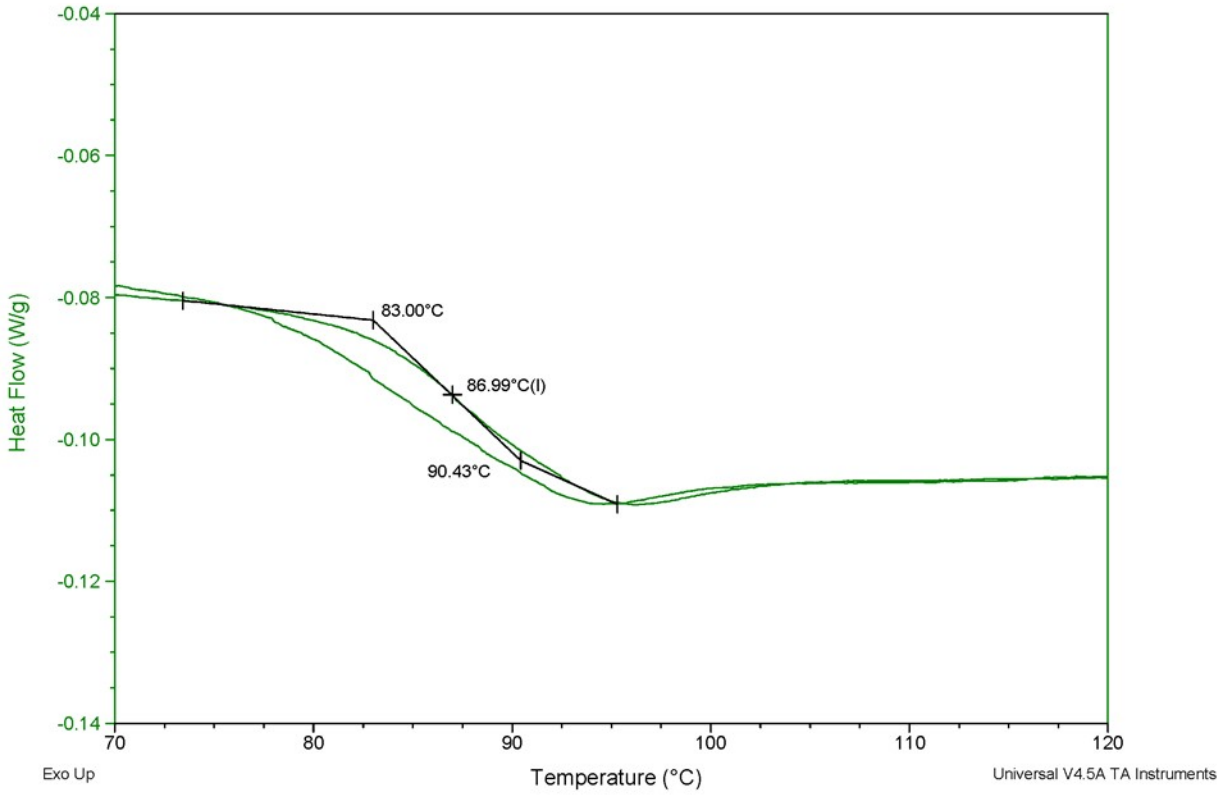


Figure S9. DSC profile of [PMDA-2MeAPI(pXy)][Tf_2N].

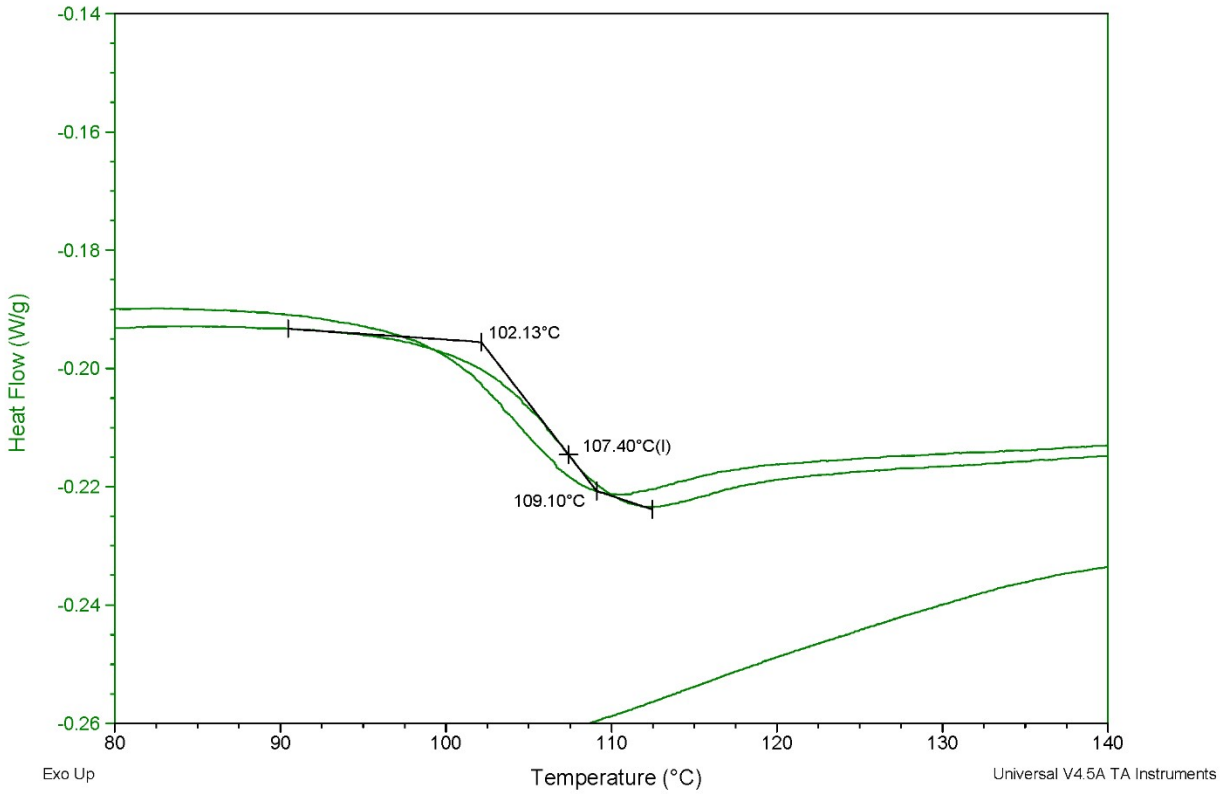


Figure S10. DSC profile of [6FDA-2MeAPI(pXy)][Tf_2N].

Table S1: Summary of DSC data for polyimide-ionenes. Values for PMDA-API and 6FDA-API from previous works.

Polyimide Ionene	**T_g (˚C)**	**$T_{d,\ onset}$ (˚C)**
[PMDA-API(pXy)][Tf_2N]	107	365
[PMDA-2MeAPI(pXy)][Tf_2N]	87	390
[6FDA-API(pXy)][Tf_2N]	94	380
[6FDA-2MeAPI(pXy)][Tf_2N]	107	410

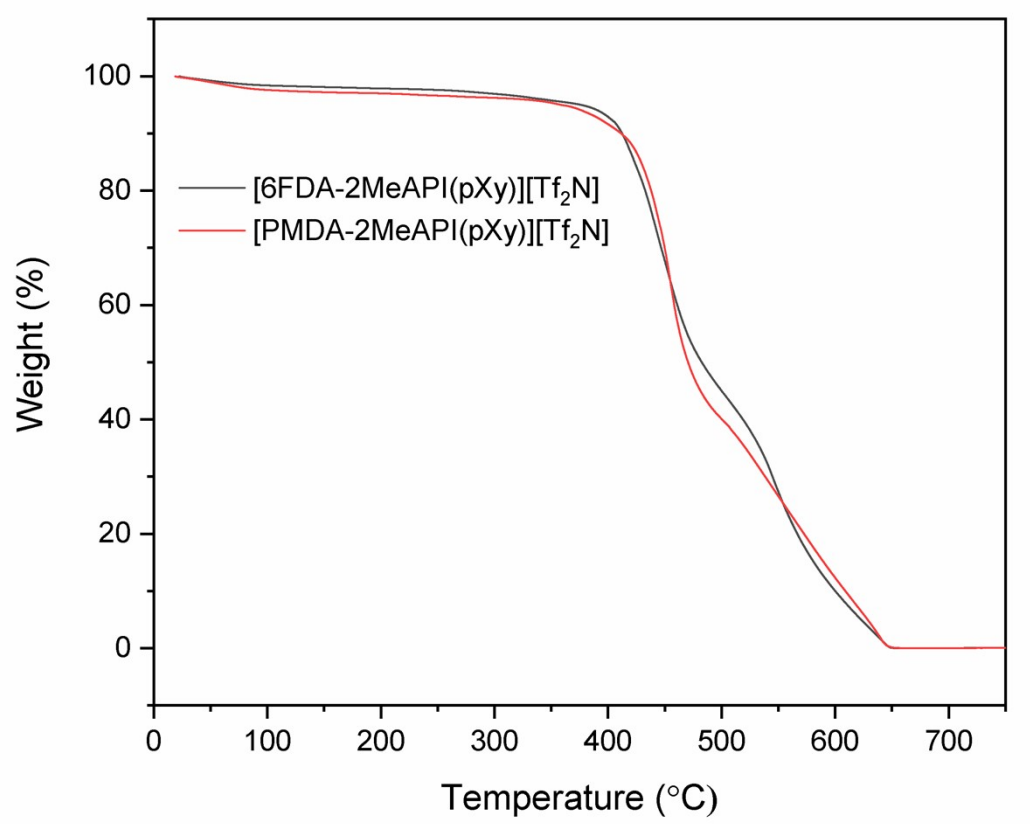


Figure S11. TGA plots of both [PMDA-2MeAPI(pXy)][Tf_2N] and [PMDA-2MeAPI(pXy)][Tf_2N].

SEM Images

Figure S12. SEM image of [PMDA-2MeAPI(pXy)][Tf_2N] + [C_4mim][Tf_2N] on a Supor ® PES support.

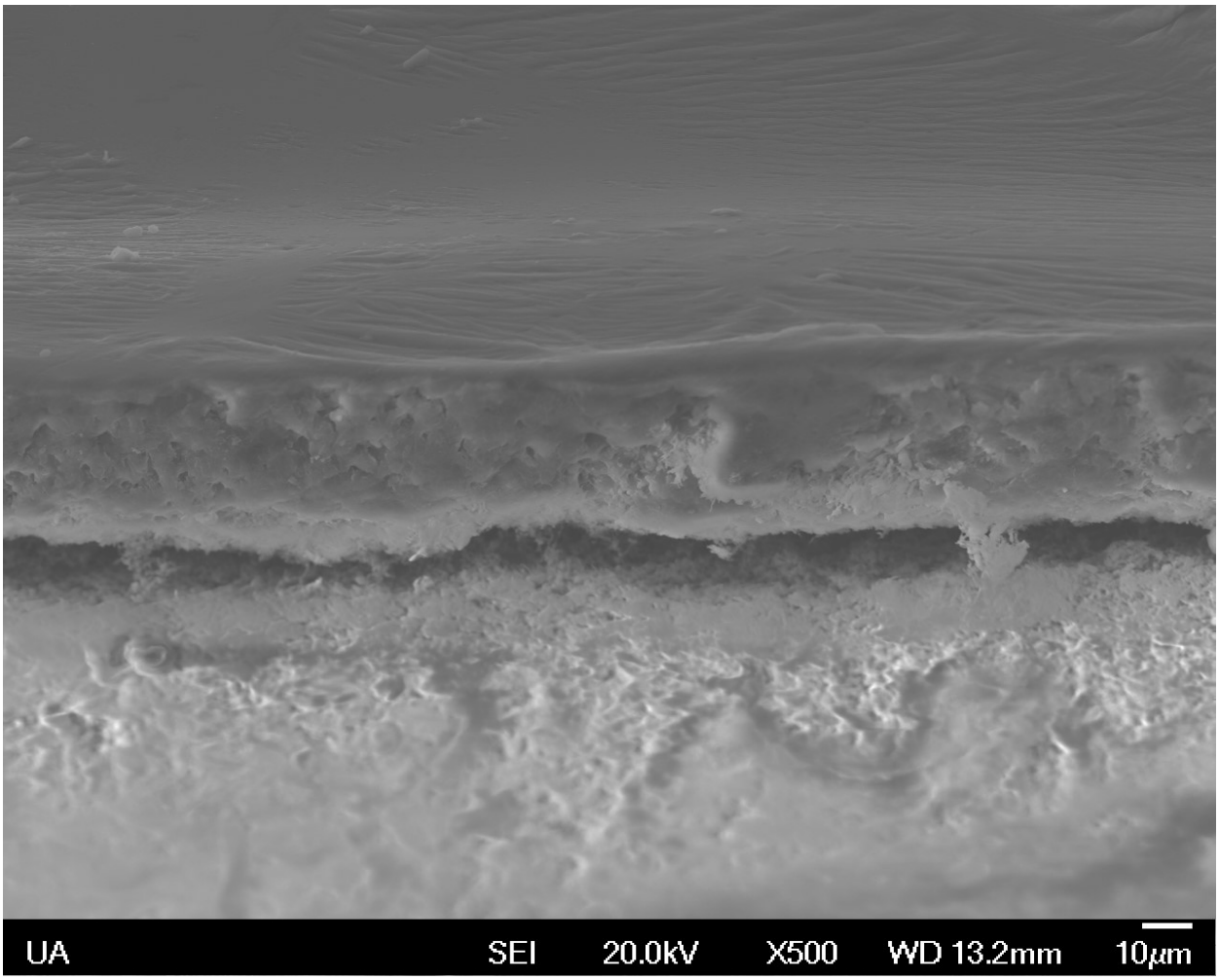
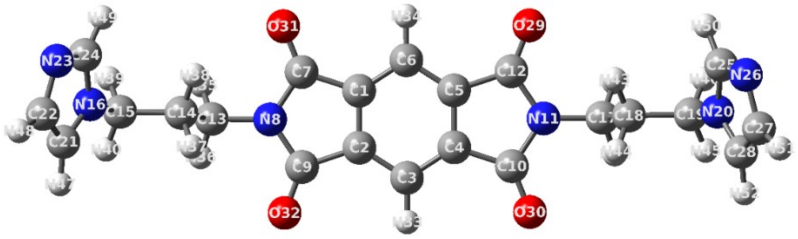
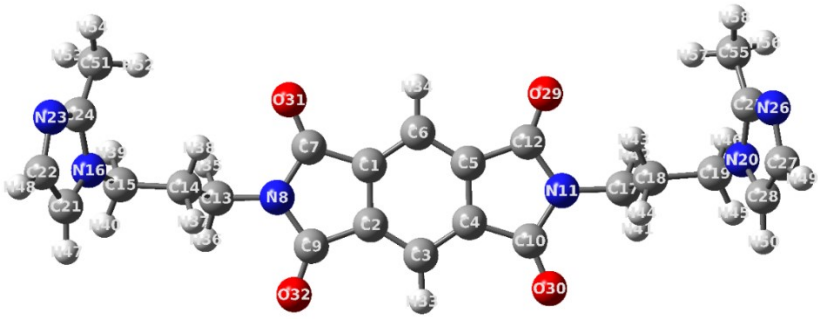


Figure S13. SEM image of [6FDA-2MeAPI(pXy)][Tf_2N] + [C_4mim][Tf_2N] on a Supor ® PES support.

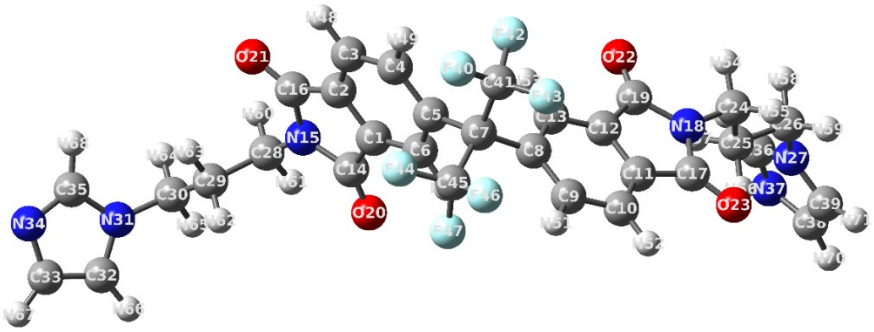
PMDA-API



PMDA-2MeAPI



6FDA-API



6FDA-2MeAPI

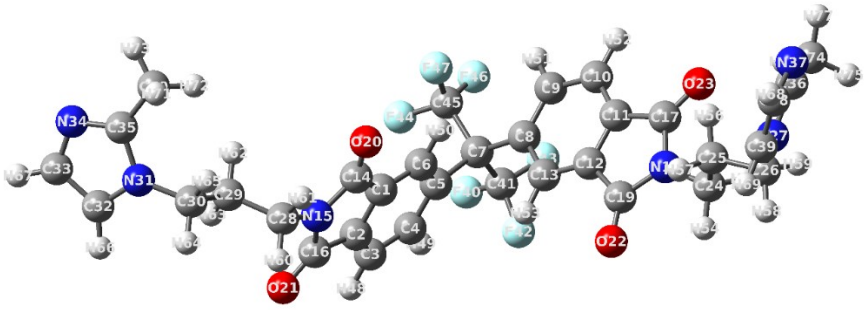


Figure S14. Optimized geometries of the studied molecules.

Table S2. Atomic charges (units of e) calculated by ChelpG and CM5 methods.*

	PMDA-API			PMDA-2MeAPI			6FDA-API			6FDA-2MeAPI		
No.	Atom	ChelpG	CM5	Atom	ChelpG	CM5	Atom	ChelpG	CM5	Atom	ChelpG	CM5
1	C	0.00	0.02	C	-0.05	0.01	C	-0.09	0.00	C	-0.10	0.00
2	C	-0.05	0.02	C	-0.03	0.01	C	-0.06	0.01	C	-0.08	0.00
3	C	-0.02	-0.03	C	-0.03	-0.03	C	-0.08	-0.05	C	-0.07	-0.05
4	C	-0.06	0.02	C	-0.04	0.01	C	-0.07	-0.06	C	-0.08	-0.06
5	C	-0.02	0.02	C	-0.05	0.01	C	0.29	0.01	C	0.34	0.00
6	C	-0.06	-0.03	C	-0.04	-0.03	C	-0.05	-0.06	C	-0.06	-0.06
7	C	0.48	0.28	C	0.52	0.28	C	-0.68	0.00	C	-0.78	0.00
8	N	-0.30	-0.25	N	-0.30	-0.26	C	0.33	0.01	C	0.30	0.00
9	C	0.51	0.28	C	0.49	0.28	C	-0.10	-0.06	C	-0.06	-0.06
10	C	0.52	0.28	C	0.50	0.28	C	-0.05	-0.05	C	-0.10	-0.05
11	N	-0.31	-0.25	N	-0.31	-0.26	C	-0.07	0.01	C	-0.05	0.00
12	C	0.50	0.28	C	0.52	0.28	C	-0.08	0.00	C	-0.12	0.00
13	C	0.13	-0.03	C	0.12	-0.03	C	-0.07	-0.06	C	-0.03	-0.06
14	C	0.06	-0.15	C	0.00	-0.15	C	0.56	0.28	C	0.57	0.27
15	C	-0.22	-0.02	C	-0.16	-0.03	N	-0.39	-0.25	N	-0.39	-0.26
16	N	0.18	-0.23	N	0.06	-0.23	C	0.55	0.28	C	0.57	0.28
17	C	0.12	-0.03	C	0.14	-0.03	C	0.53	0.28	C	0.56	0.28
18	C	0.06	-0.15	C	0.02	-0.15	N	-0.32	-0.25	N	-0.34	-0.26
19	C	-0.21	-0.02	C	-0.18	-0.03	C	0.54	0.28	C	0.56	0.28
20	N	0.18	-0.23	N	0.07	-0.23	O	-0.39	-0.25	O	-0.41	-0.26
21	C	-0.21	0.11	C	-0.18	0.11	O	-0.39	-0.24	O	-0.41	-0.25
22	C	0.36	0.12	C	0.32	0.11	O	-0.39	-0.24	O	-0.40	-0.25
23	N	-0.47	-0.31	N	-0.51	-0.32	O	-0.38	-0.24	O	-0.42	-0.25
24	**C**	**0.28**	**0.23**	**C**	**0.55**	**0.29**	C	0.13	-0.03	C	0.13	-0.03
25	**C**	**0.27**	**0.23**	**C**	**0.55**	**0.29**	C	0.07	-0.15	C	0.01	-0.15
26	N	-0.47	-0.31	N	-0.52	-0.32	C	-0.20	-0.02	C	-0.11	-0.03
27	C	0.36	0.12	C	0.32	0.11	N	0.18	-0.23	N	0.06	-0.23
28	C	-0.20	0.11	C	-0.18	0.11	C	0.20	-0.03	C	0.21	-0.03
29	O	-0.36	-0.23	O	-0.39	-0.25	C	0.10	-0.15	C	0.05	-0.15
30	O	-0.36	-0.23	O	-0.37	-0.23	C	-0.29	-0.02	C	-0.22	-0.03
31	O	-0.36	-0.23	O	-0.39	-0.25	N	0.21	-0.23	N	0.07	-0.23
32	O	-0.36	-0.22	O	-0.37	-0.23	C	-0.23	0.09	C	-0.19	0.10

33	H	0.13	0.15	H	0.13	0.14	C	0.34	0.11	C	0.29	0.11
34	H	0.14	0.15	H	0.13	0.14	N	-0.47	-0.32	N	-0.52	-0.32
35	H	0.07	0.13	H	0.07	0.13	**C**	**0.25**	**0.22**	**C**	**0.55**	**0.29**
36	H	0.06	0.13	H	0.07	0.13	**C**	**0.26**	**0.22**	**C**	**0.56**	**0.29**
37	H	0.03	0.11	H	0.05	0.11	N	-0.48	-0.32	N	-0.52	-0.32
38	H	0.01	0.11	H	0.01	0.10	C	0.35	0.11	C	0.30	0.10
39	H	0.10	0.14	H	0.08	0.13	C	-0.23	0.10	C	-0.20	0.10
40	H	0.15	0.14	H	0.14	0.14	F	-0.14	-0.09	F	-0.14	-0.09
41	H	0.07	0.13	H	0.06	0.13	C	0.63	0.34	C	0.63	0.34
42	H	0.08	0.13	H	0.07	0.13	F	-0.17	-0.10	F	-0.17	-0.10
43	H	0.01	0.11	H	0.00	0.10	F	-0.17	-0.10	F	-0.16	-0.10
44	H	0.03	0.11	H	0.05	0.11	F	-0.16	-0.10	F	-0.17	-0.10
45	H	0.15	0.14	H	0.15	0.14	C	0.60	0.34	C	0.61	0.34
46	H	0.10	0.14	H	0.09	0.13	F	-0.13	-0.09	F	-0.13	-0.09
47	H	0.21	0.17	H	0.21	0.17	F	-0.17	-0.10	F	-0.17	-0.10
48	H	0.10	0.17	H	0.11	0.16	H	0.14	0.14	H	0.14	0.14
49	H	0.15	0.17	H	0.11	0.16	H	0.14	0.12	H	0.14	0.12
50	H	0.15	0.17	H	0.21	0.17	H	0.06	0.12	H	0.07	0.12
51	H	0.10	0.17	C	-0.39	-0.19	H	0.15	0.12	H	0.14	0.12
52	H	0.21	0.17	H	0.16	0.12	H	0.14	0.14	H	0.14	0.13
53				H	0.17	0.14	H	0.08	0.12	H	0.07	0.12
54				H	0.17	0.14	H	0.07	0.13	H	0.06	0.13
55				C	-0.40	-0.19	H	0.06	0.13	H	0.07	0.12
56				H	0.17	0.14	H	0.03	0.11	H	0.00	0.10
57				H	0.16	0.12	H	0.00	0.11	H	0.04	0.11
58				H	0.17	0.14	H	0.09	0.13	H	0.13	0.13
59							H	0.14	0.14	H	0.06	0.13
60							H	0.05	0.13	H	0.03	0.13
61							H	0.03	0.13	H	0.04	0.13
62							H	0.02	0.11	H	0.01	0.10
63							H	0.00	0.11	H	0.04	0.11
64							H	0.11	0.13	H	0.15	0.13
65							H	0.16	0.13	H	0.09	0.13
66							H	0.21	0.16	H	0.21	0.16
67							H	0.10	0.16	H	0.11	0.16
68							H	0.15	0.17	H	0.11	0.16

69	H	0.14	0.17	H	0.21	0.16
70	H	0.10	0.16	C	-0.42	-0.20
71	H	0.21	0.16	H	0.17	0.13
72				H	0.16	0.12
73				H	0.17	0.14
74				C	-0.42	-0.20
75				H	0.16	0.13
76				H	0.17	0.12
77				H	0.17	0.14

*The C atoms shown in bold are the C(2) sites, which are linked with the substituted -H atoms or -CH_3 atoms.

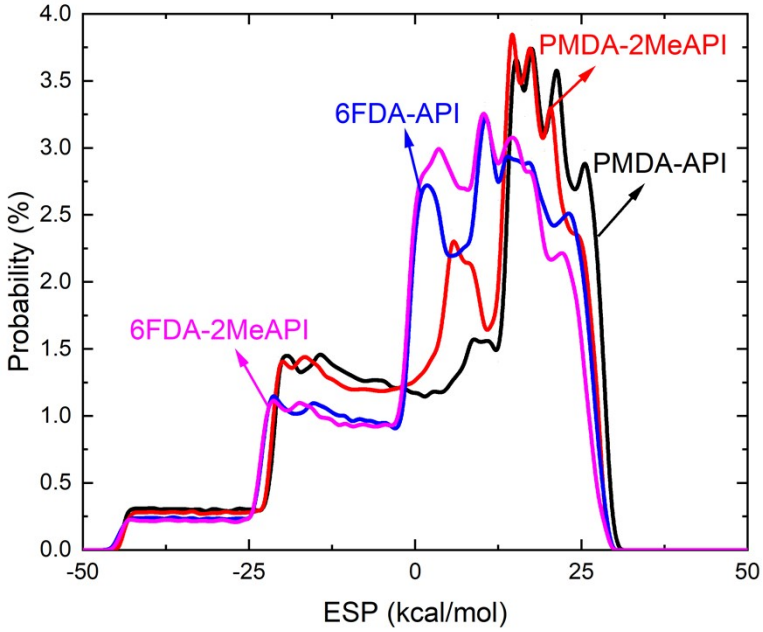
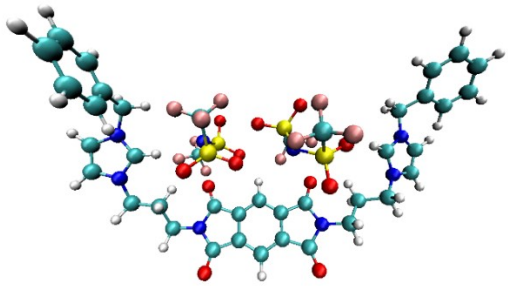
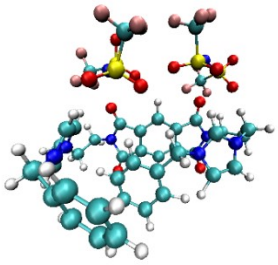
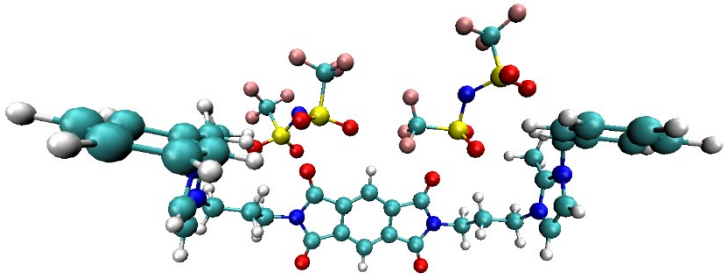
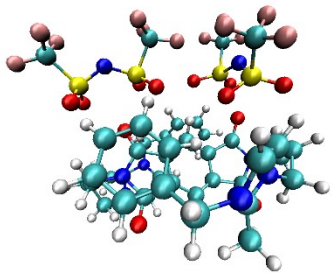


Figure S15. Electrostatic potential distribution (units of kcal/mol) of studied molecules.

Table S3. General interaction properties function (GIPF) descriptors of studied molecules.

	SA	V_{ion}	V	V_{min}	V_{max}	Π	σ_{tot}^2
	Å^2	Å^3	kcal/mol				(kcal/mol)^2
PMDA-API	459	497	5.6	-15.3	16.8	15.0	166
PMDA-2MeAPI	494	542	4.8	-15.1	15.0	13.8	161
6FDA-API	601	684	4.9	-15.2	13.4	12.6	177
6FDA-2MeAPI	635	729	4.4	-14.8	12.4	11.9	171

First frame	Last frame
PMDA-API	
	
PMDA-2MeAPI	
	
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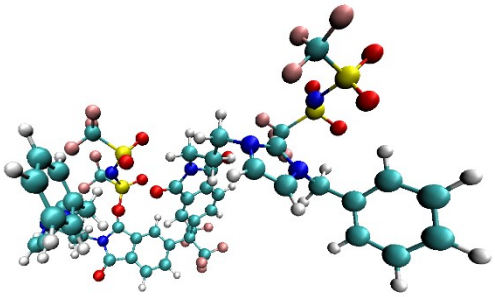	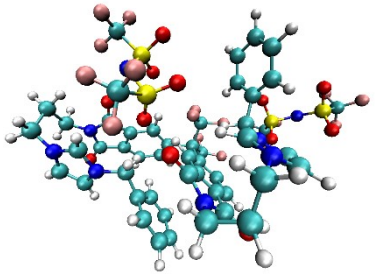
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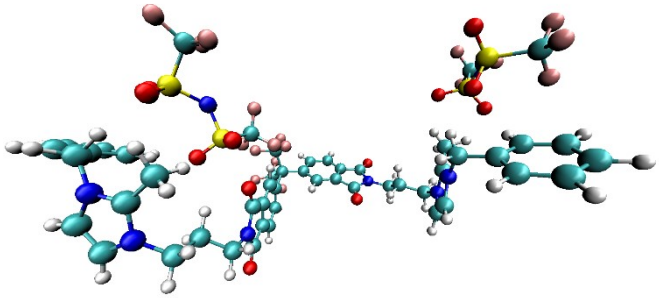	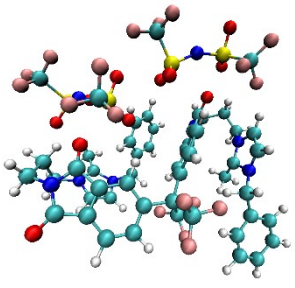

Figure S16. Representative snapshots of the studied monomers during MD simulations.

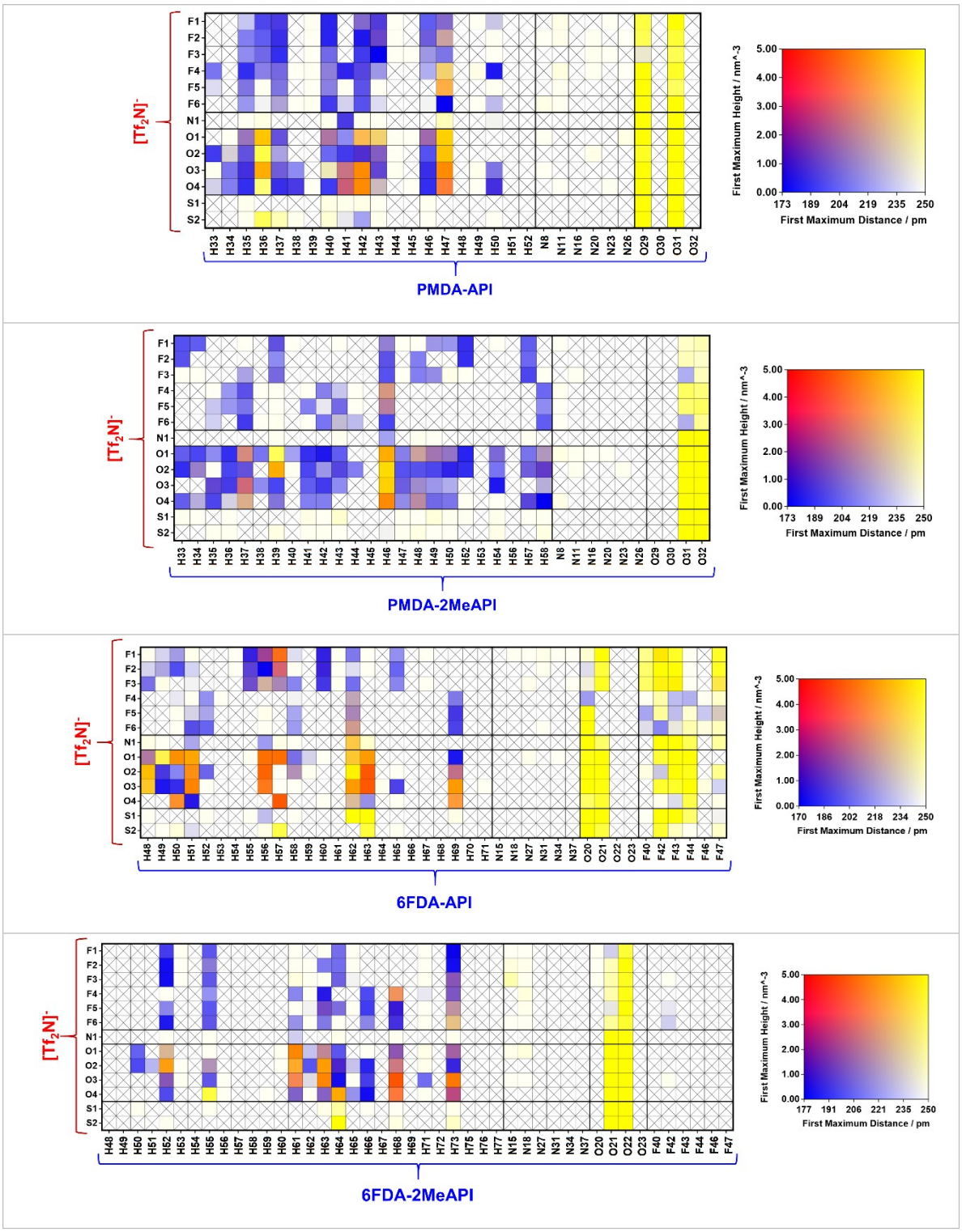

Figure S17. Connection matrices (CMats) for all non-carbon atoms within the monomers, taken from the MD simulations. The color in each square represents both the peak height and the distance to the first maximum in the corresponding radial distribution function (for color scale, see the right-hand side). The individual grids are labeled according to the assignments shown in Table S1.

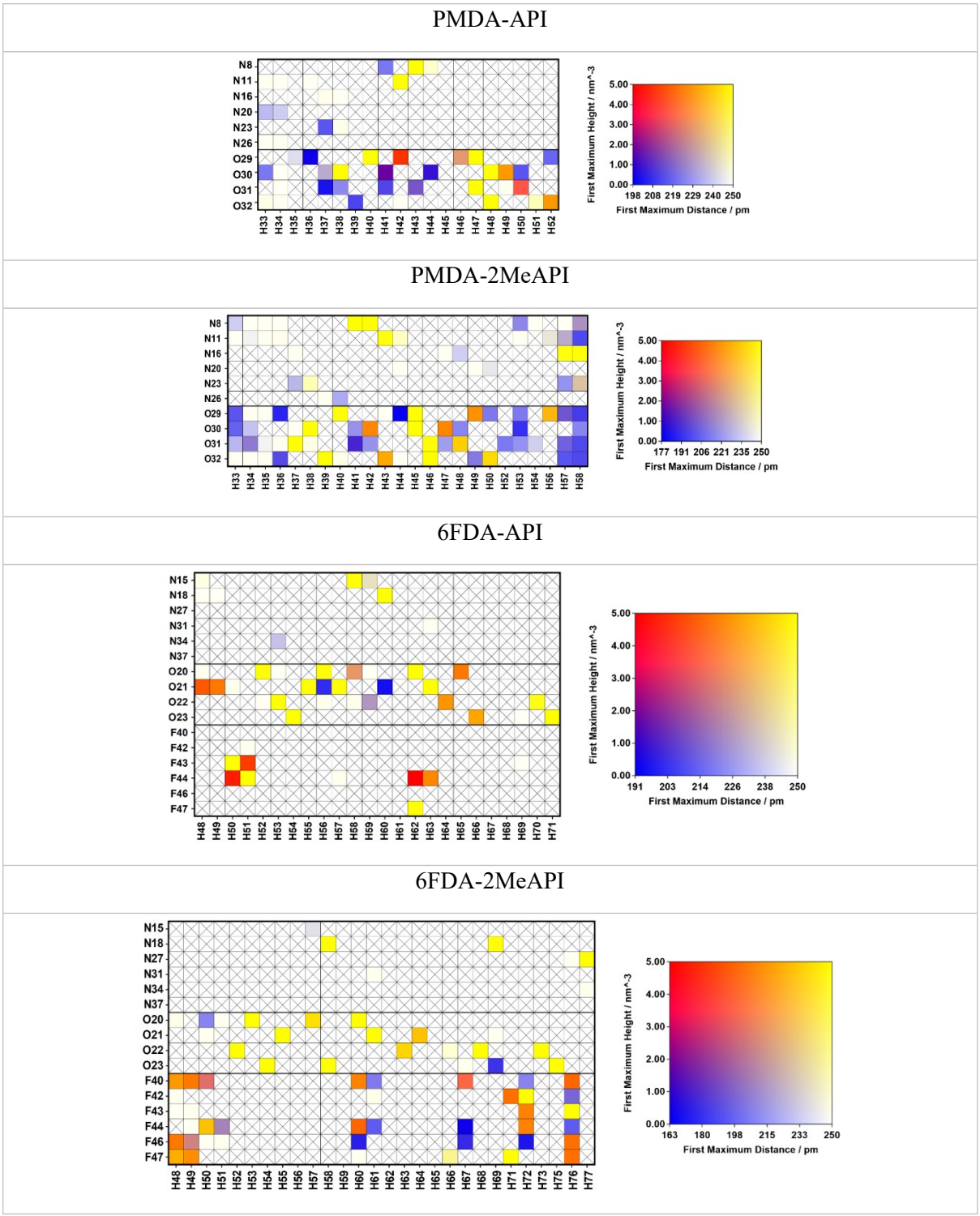

Figure S18. Intramolecular connection matrices (CMats) for all non-carbon atoms within the positively charged monomers, taken from the MD simulations. Rows represent hydrogen bond acceptors, and columns correspond to hydrogen bond donors. The color in each square represents both the peak height and the distance to the first maximum in the corresponding radial distribution function (for color scale, see the right-hand side). The individual grids are labeled according to the assignments shown in Table S1.

Robeson Plots

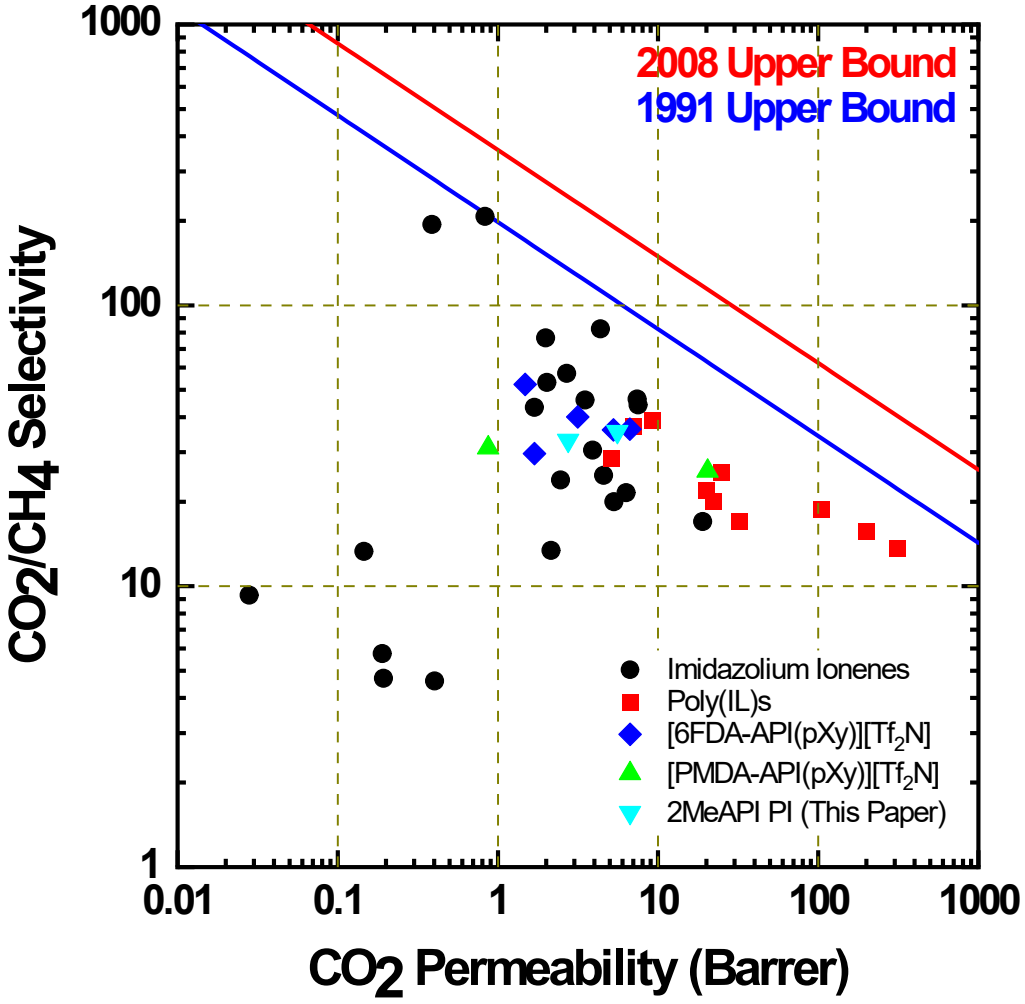

Figure S19. CO_2/CH_4 Robeson plot of [6FDA-2MeAPI(pXy)][Tf_2N] + [C_4mim][Tf_2N] and [6FDA-2MeAPI(pXy)][Tf_2N] + [C_4mim][Tf_2N] along with other ionic materials.

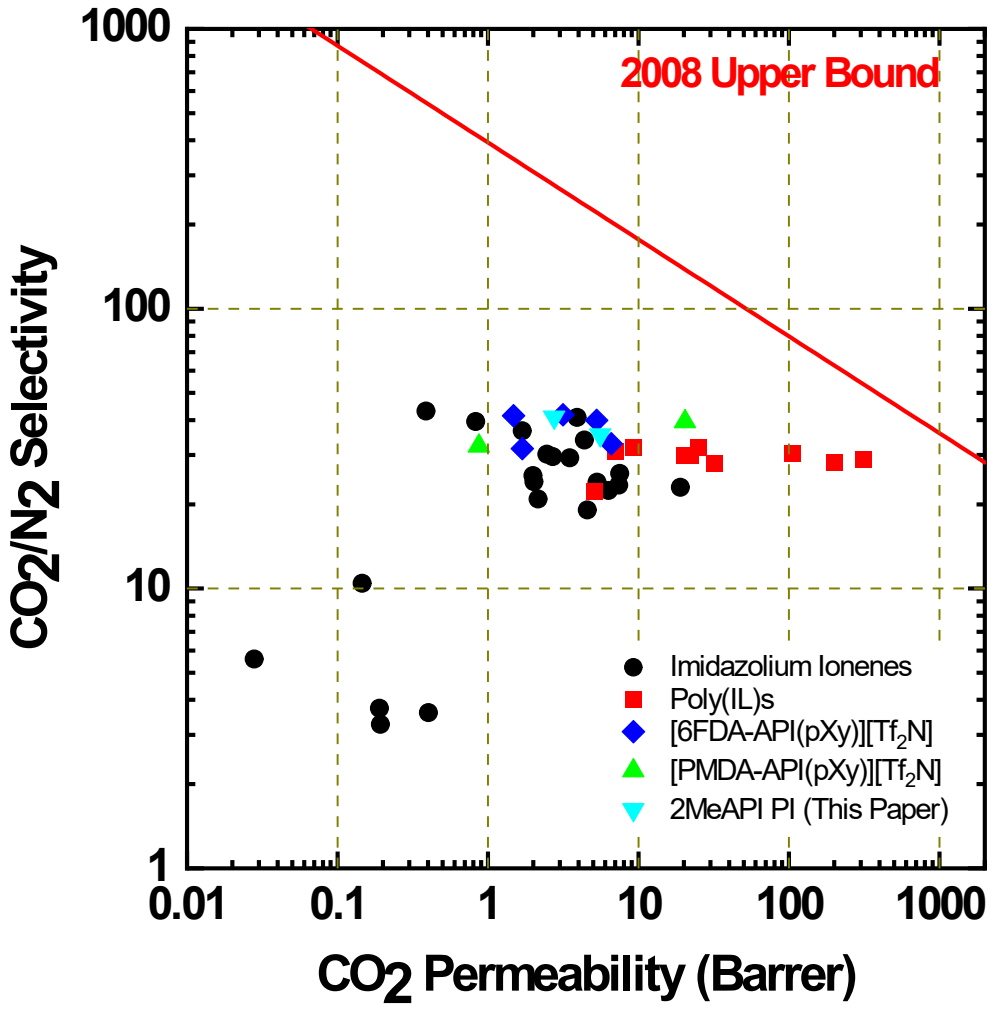

Figure S20. CO_2/N_2 Robeson plot of [6FDA-2MeAPI(pXy)][Tf_2N] + [C_4mim][Tf_2N] and [6FDA-2MeAPI(pXy)][Tf_2N] + [C_4mim][Tf_2N] along with other ionic materials.