Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for publication

Improved TTF functionalization of polymers for two-dimensional charge-transfer networks

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I. UV-Vis spectra and TTF functionalization calculation based on UV-Vis spectra

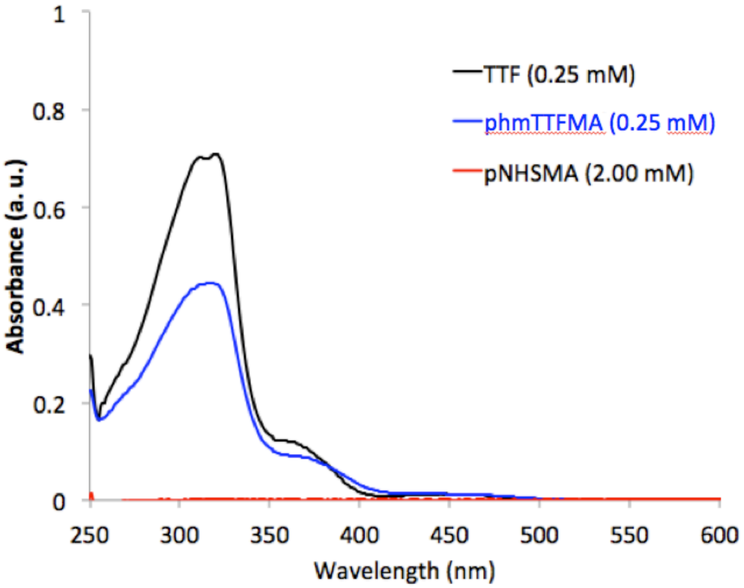


Figure S1. UV-Vis absorbance spectra of TTF (0.25 mM), phmTTFMA(0.25 mM), and pNHSMA (2.00 mM) in DMSO.

As shown in Fig. S1, the maximum absorbance peak of TTF and phmTTFMA are identical (320 nm), whereas the much more concentrated pNHSMMA shows little to none absorbance around that region. Thus, we can use Beer's law to determine how much TTF was incorporated into the polymer during the PPM process.

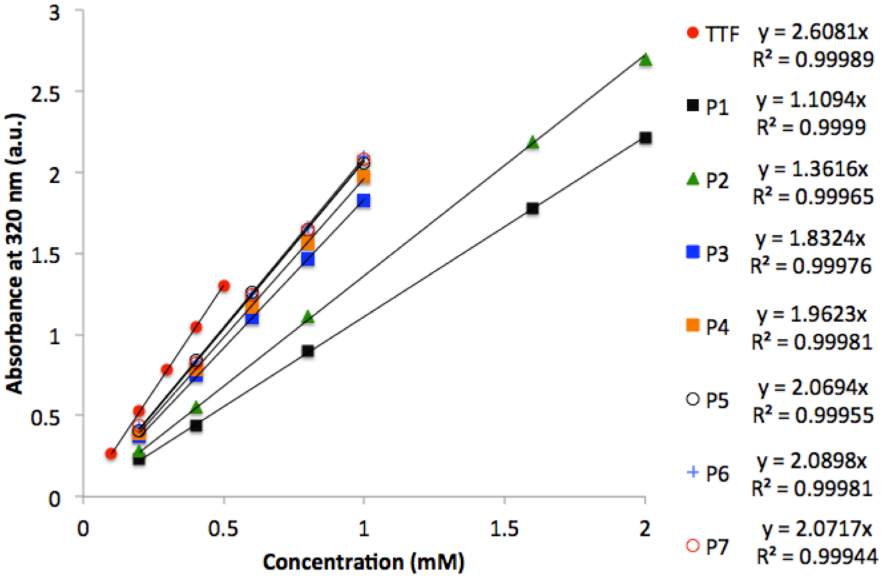


Figure S2. Calibration curve of TTF in DMSO and its comparisons with phmTTFMA, **P1** to **P7**, where 100% TTF substitution was assumed.

As shown in Fig. S2, the concentrations of phmTTFMA in DMSO are calculated under the assumption that 100% conversion from NHS to TTF was achieved. However, based on the slope of the trendline for each series, we determined that the actual % conversion is lower than 100%. For example, for 100 mol. equiv. of **P1**, only 1.1094/2.6081 = 42.54 mol was phmTTFMA. Since the molecular weight of hmTTFMA monomer (302.44 g/mol) differs from that of NHSMA monomer (183.16 g/mol), the mol. equiv. of unreacted pNHSMA is (100-42.54)x302.44/183.16 = 94.93 mol. Thus, the actual % TTF functionalization is 42.54/(42.54+94.93) = 31%. Analogously, we can determine the % TTF functionalization for **P2-P11**.

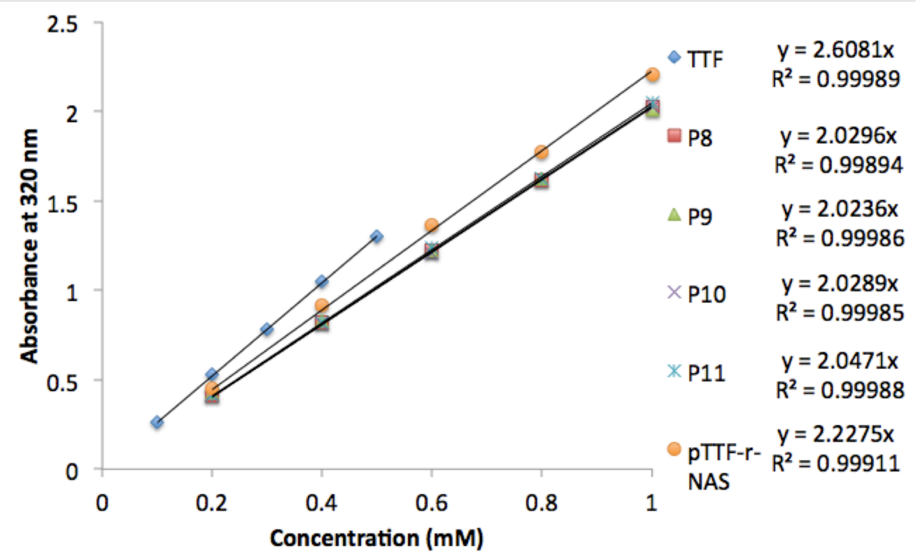
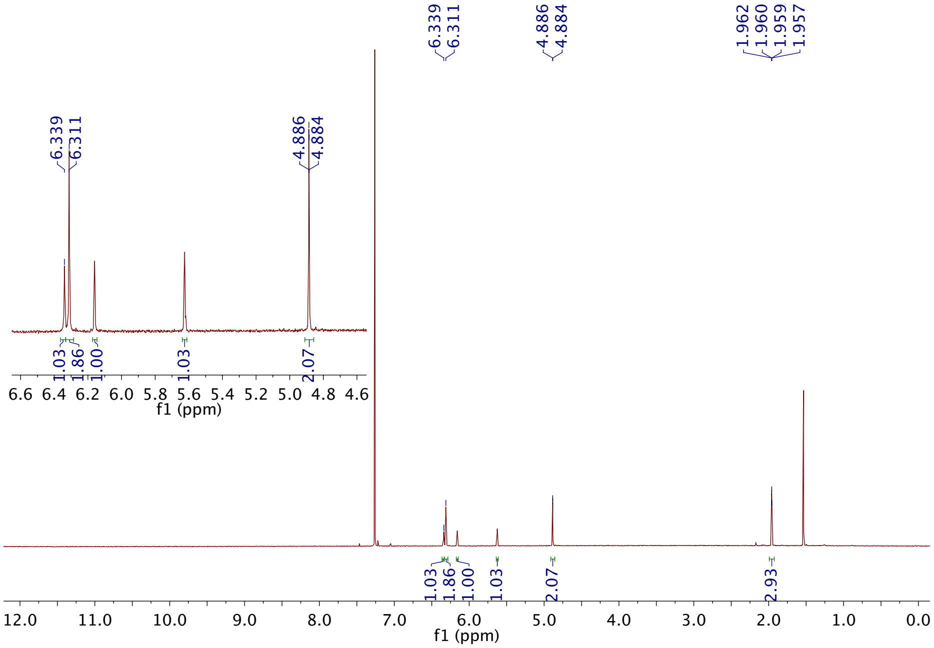


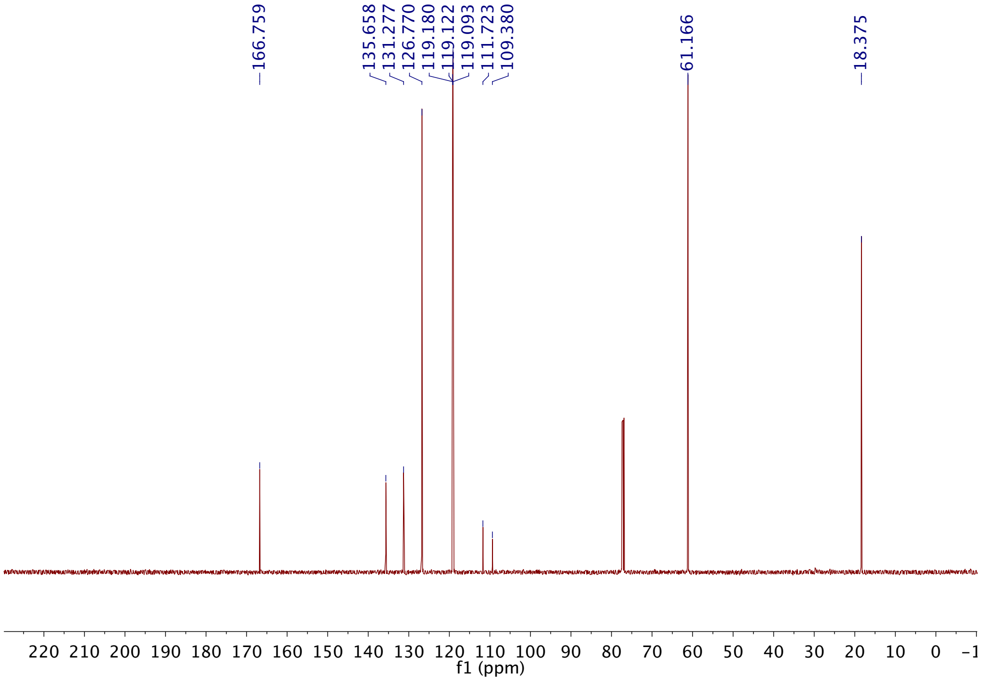
Figure S3. Calibration curve of TTF in DMSO and its comparision with phmTTFMA, **P8** to **P11**, where 100% TTF subsitution was assumed.

II. NMR spectra and TTF functionalization calculation based on ^{1}H NMR integration

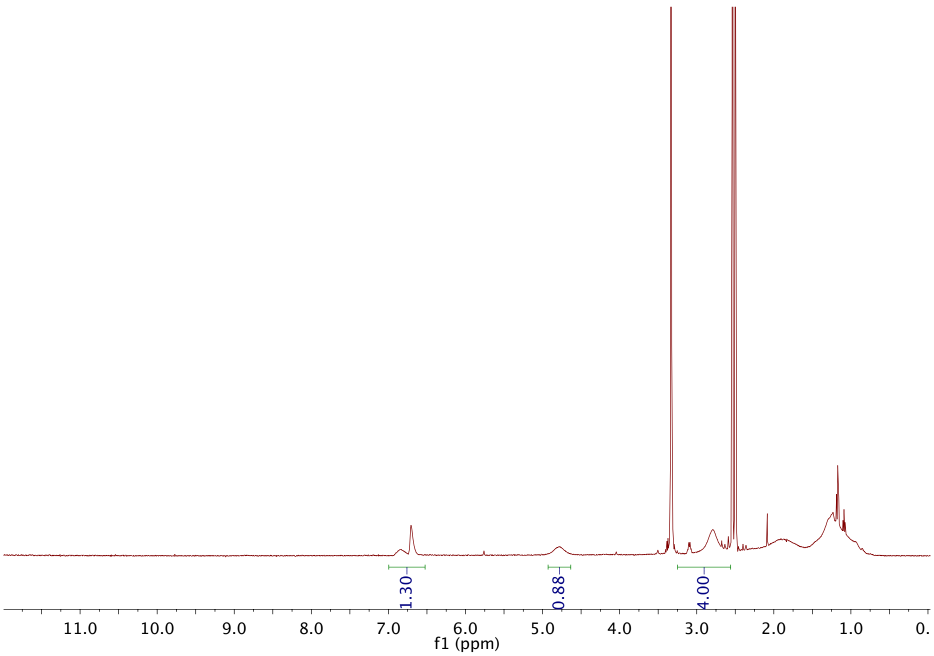
^{1}H NMR of compound 1



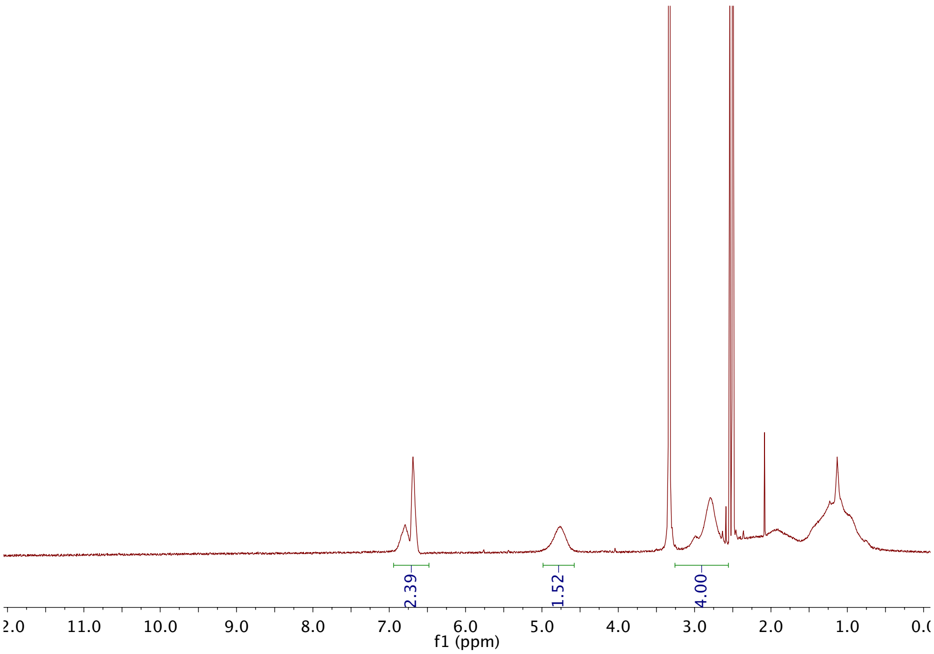
^{13}C NMR of compound 1



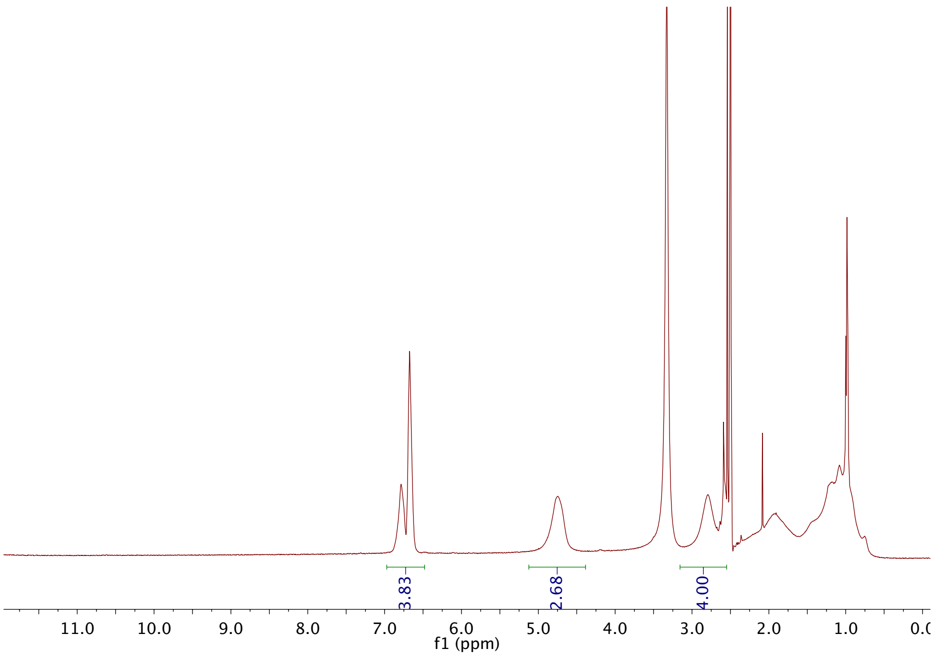
^{1}H NMR of P1:



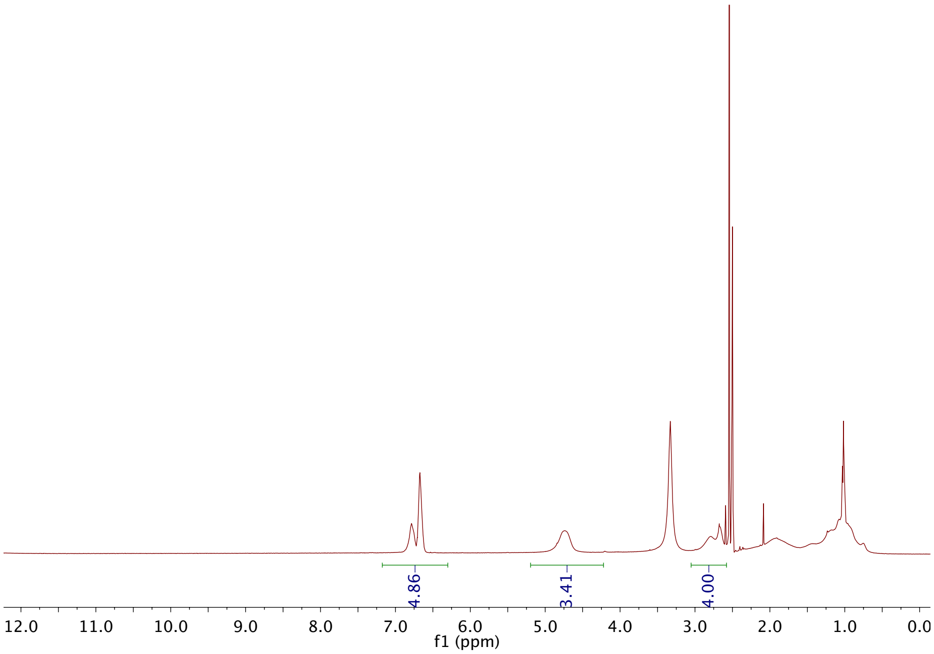
^{1}H NMR of P2:



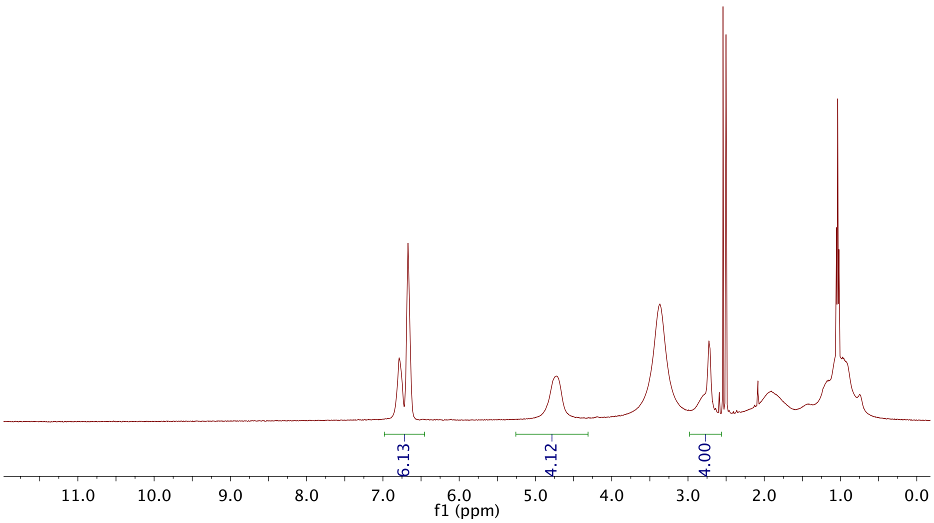
^{1}H NMR of P3:



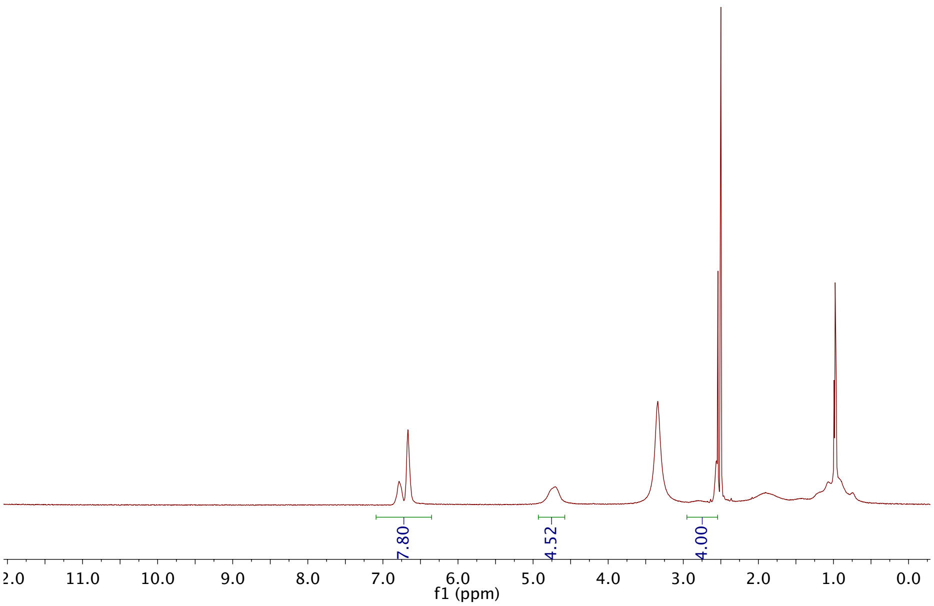
^{1}H NMR of P4:



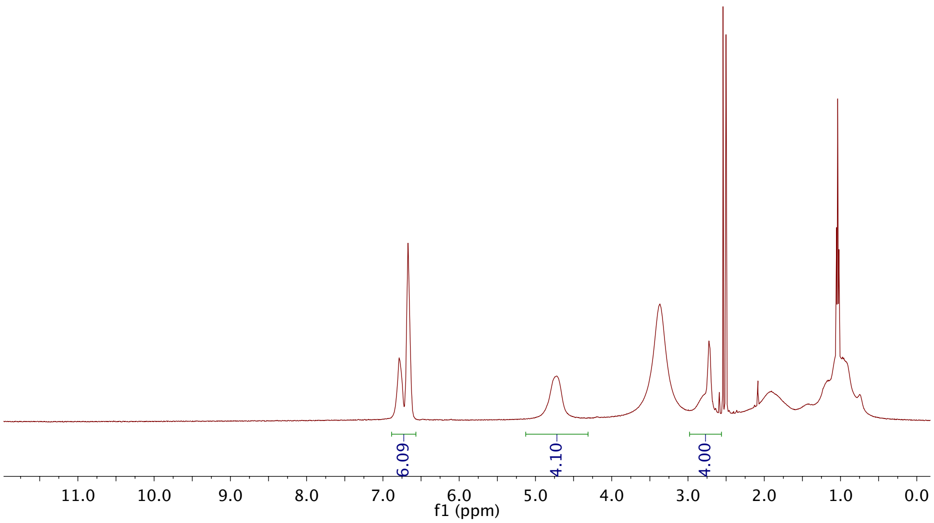
^{1}H NMR of P5:



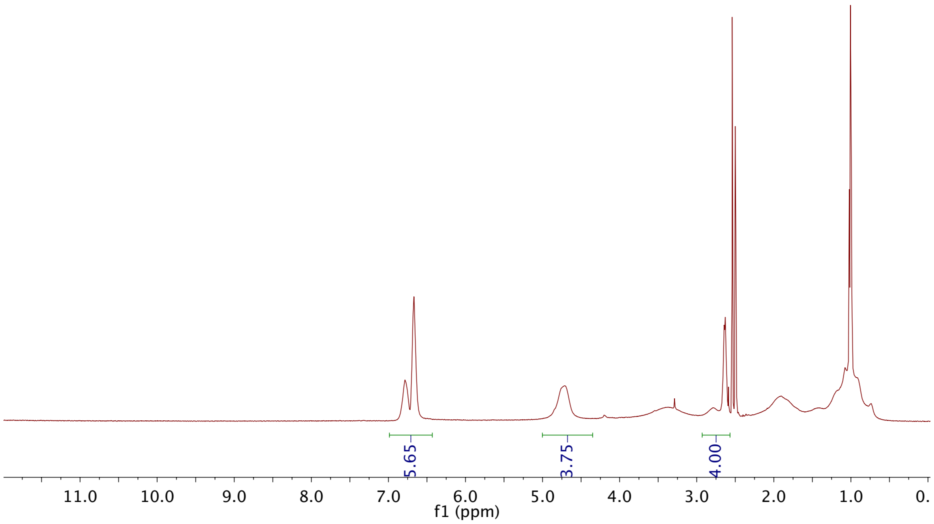
^{1}H NMR of P6:



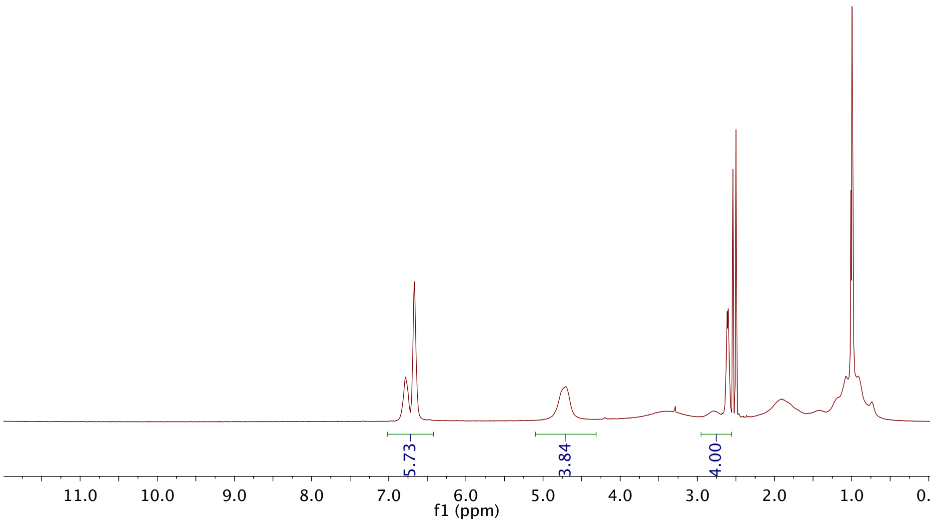
^{1}H NMR of P7:



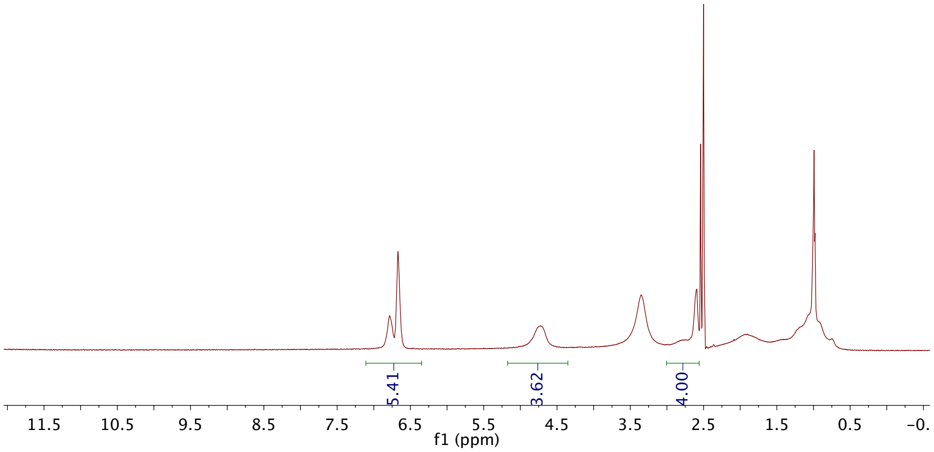
^{1}H NMR of P8:



^{1}H NMR of P9:



^{1}H NMR of P10:



^{1}H NMR of P11:

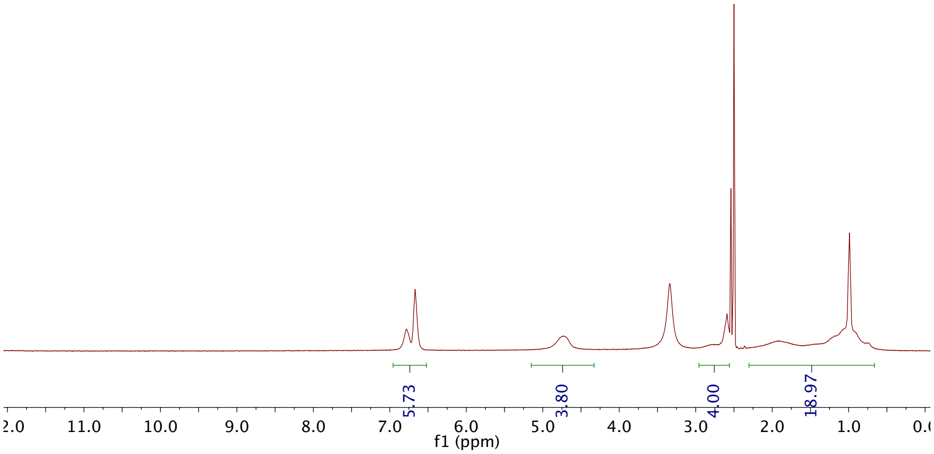


Table S1. Relative proton integration values of **P1** to **P11** from ^{1}H NMR spectra.

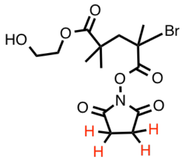
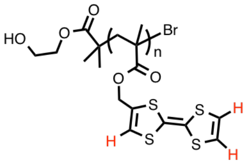
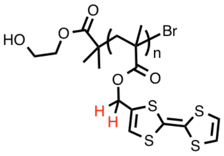
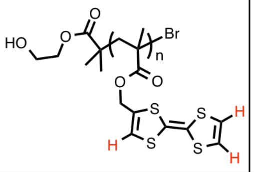
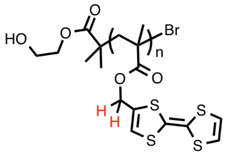
Relative proton integration value from ^{1}H NMR	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**	**P11**
	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
	1.30	2.39	3.83	4.86	6.13	7.80	6.09	5.65	5.73	5.41	5.73
	0.88	1.52	2.68	3.41	4.12	4.52	4.10	3.75	3.84	3.62	3.80

Table S2. Percent TTF functionalization of the obtained polymer (**P1** to **P11**) after PPM based on relative proton integration values.

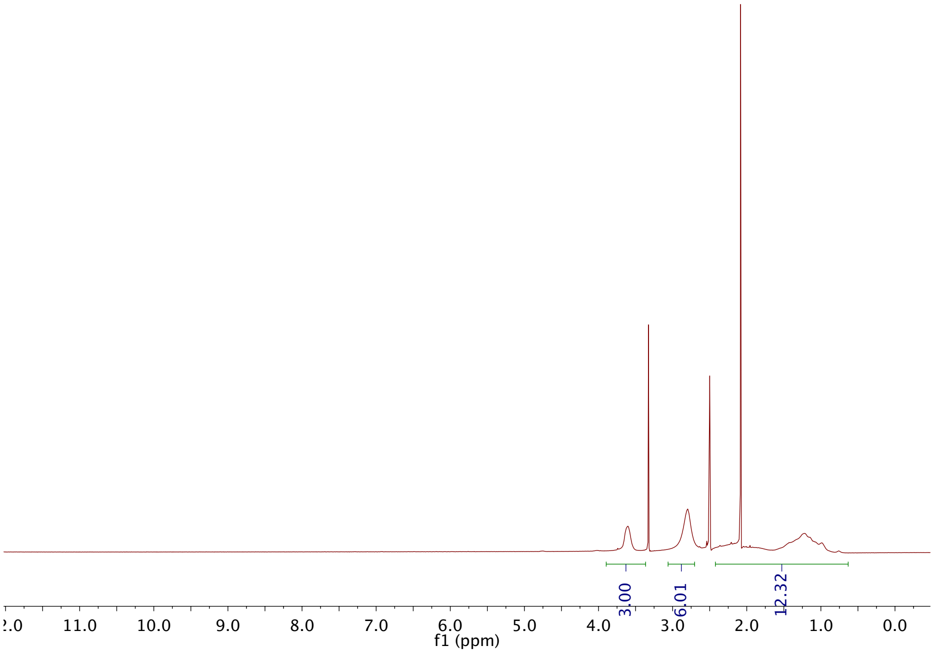
% TTF functionalization based on H integration	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**	**P11**
	30	44	56	62	67	72	67	65	66	64	66
	31	43	57	63	67	69	67	65	66	65	66

Sample calculation of %TTF functionalization of **P1**.

%TTF functionalization of **P1** based on TTF proton = (1.3/3)/(1.3/3+4/4)x100% = 30%.

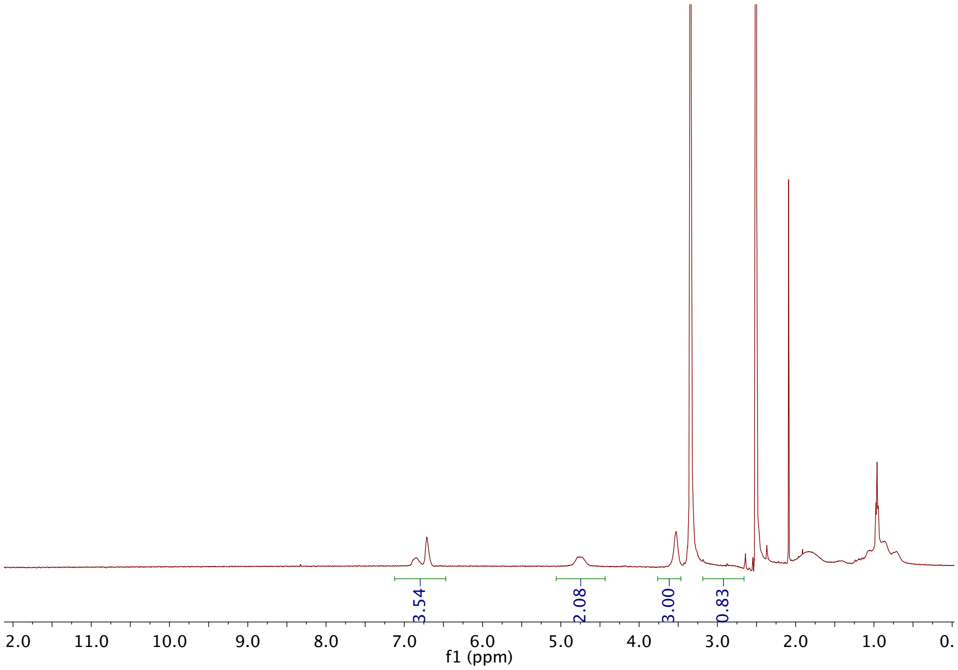
%TTF functionalization of **P1** based on -OCH$_2$- = (0.88/2)/(0.88/2+4/4)x100% = 31%

^{1}H NMR of p(NHSMA$_{60}$-co-MMA$_{40}$)



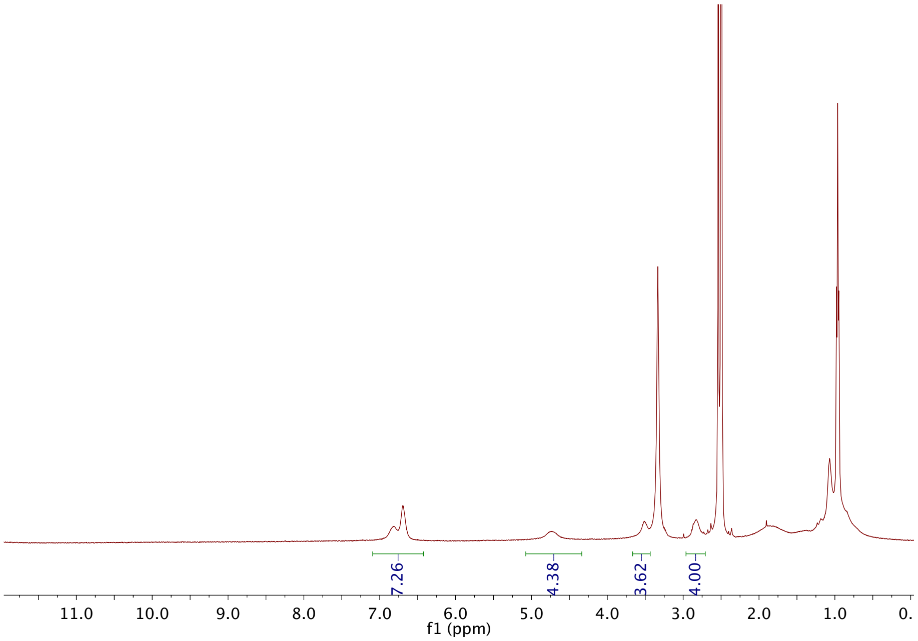
Based on the relative proton integration value, we can determine that the molar ratio between MMA and NHSMA in the copolymer is 2:3 (as calculated by (3/3) : (6/4)).

^{1}H NMR of p(hmTTFMA$_{60}$-co-MMA$_{40}$)(TTF functionalized polymer from p(NHSMA$_{60}$-co-MMA$_{40}$)



Analogous to the calculations for **P1** to **P11**, % TTF functionalization for **phmTTFMA-co-MMA** was determined to be 85 mol% (based on relative proton integration value on TTF) and 83 % (based on proton integration value on –OCH$_2$–).

^{1}H NMR of p(hmTTFMA-co-MMA) (Obtained polymer from p10 reacted with methanol)



Based on the analysis of ^{1}H NMR spectra, proton TTF/(NHS+TTF) ratio increased from 64% to 71% after subjecting phmTTFMA (**P10**) with methanol. Additional methyl peak from MMA appeared which is consistent the ^{1}H NMR spectrum of phmTTFMA-co-MMA (TTF functionalized polymer from p($NHSMA_{60}$-co-MMA_{40}). This indicated that the remaining NHS group in phmTTFMA(**P10**) remains active and is be replaced by methoxy, a less sterically congested group.

III. Elemental analysis data and TTF functionaization calculation based on weight percent of sulfur and nitrogen

Table S3. Elemental analysis results of sulfur and nitrogen for **P1** to **P11**.

Weight % from elemental analysis	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11
S analysis	18.06	20.88	30.57	32.66	34.32	34.35	34.00	33.66	33.63	33.33	33.30
N analysis	4.22	3.41	2.13	1.76	1.46	1.58	1.57	1.64	1.70	1.82	1.76

Table S4. Percent TTF functionalization of the obtained polymer (**P1** to **P11**) after PPM based on elemental analysis data.

% TTF functionalization based on elemental analysis	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11
S analysis	31	37	61	67	72	72	71	70	70	69	69
N analysis	33	43	61	67	72	70	70	69	68	66	67

Sample calculation of %TTF functionalization of **P1**.

%TTF functionalization of **P1** based on S:

$$\frac{4 * 32.06x}{302.44x + 183.16(1-x)}100\% = 18.06$$

Solve for x, where x = 31.

%TTF functionalization of **P1** based on N:

$$\frac{14.01y}{302.44(1-y)+183.16y}100\% = \ 4.22$$

Solve for y, where y = 67. % TTF functionalization = 100-67 = 33.

Elemental analysis data of **p(NHSMA$_{60}$-co-MMA$_{40}$)**:C(54.46); H(5.59); N (5.61).

Elemental analysis data of **phmTTFMA -co-MMA**: S (30.24); C(47.50); H(4.40); N (0.73).

Analogous to the calculations for **P1** to **P11**, % TTF functionalization for **phmTTFMA-co-MMA** was determined to be 82 mol %

Elemental analysis data of **p(NAS)**:C(49.71); H(4.24); N (8.26).

Elemental analysis data of **phmTTFA-r-NAS**: S (37.98); C (43.01); H(3.03); N (1.12).

Analogous to the calculations for **P1** to **P11**, % TTF functionalization for **phmTTFMA-co-MMA** was determined to be 78 mol %

IV. IR of phmTTFMA and phmTTFMA-co-MMA from PPM using pNHSMA-co-MMA and phmTTFMA as polymer precursors

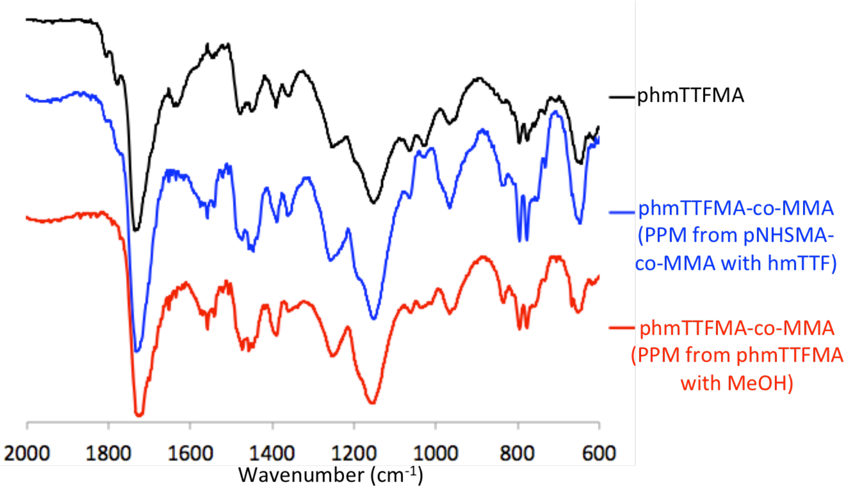
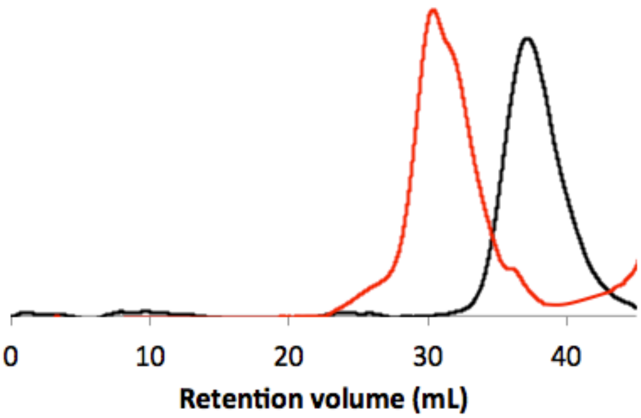


Figure S4. IR spectra of phmTTFMA and phmTTFMA-co-MMA from PPM using different polymer precursors.

V. GPC data



p(hmTTFMA$_{60}$ -co-MMA$_{40}$) (TTF functionalized polymer from p(NHSMA$_{60}$-r-MMA$_{40}$) (black curve)

Mn = 20.7 kDa, PDI = 1.24

pTTFA-co-NAS (TTF functionalized polymer from pNAS) (red curve)

Mn = 44.5 kDa, PDI = 1.67

VI. TGA data of 4-(hydroxymethyl)TTF

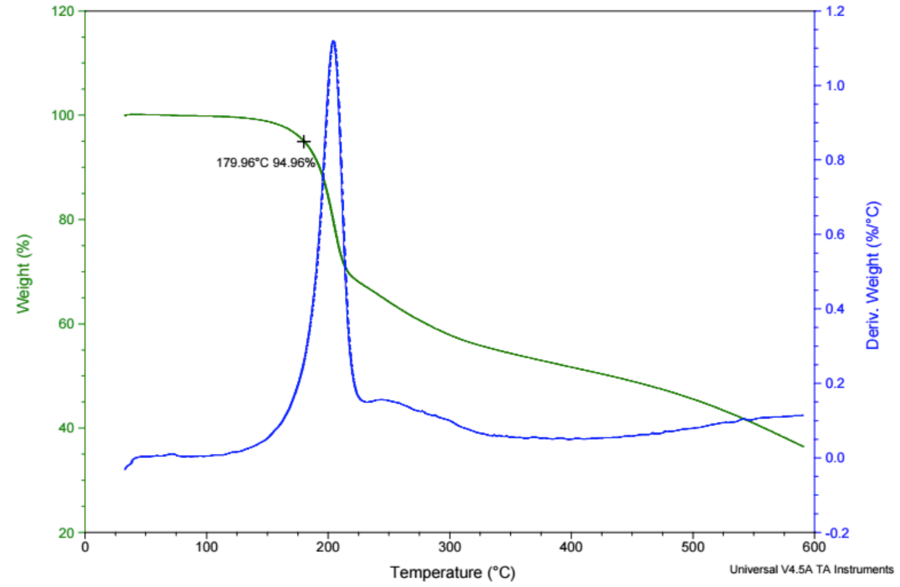


Figure S5. TGA curve of 4-(hydroxymethyl)TTF where T_d = 179 °C at 5 % weight loss with a heating rate of 10 °C min^{-1}.

VII. XRD data

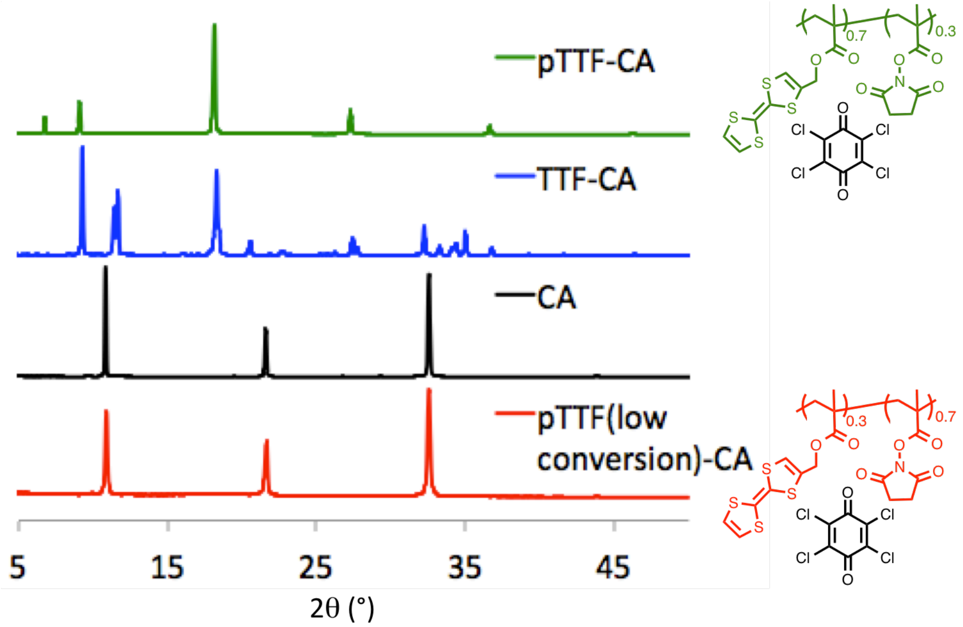


Figure S6. X-ray patterns of the cast films of pTTF-CA (both low and high % TTF functionalization), TTF-CA, CA. When TTF incorporation to the polymer backbone is decreased, phase separation between pTTF and chloranil was observed.

VIII. Film-forming phmTTFMA

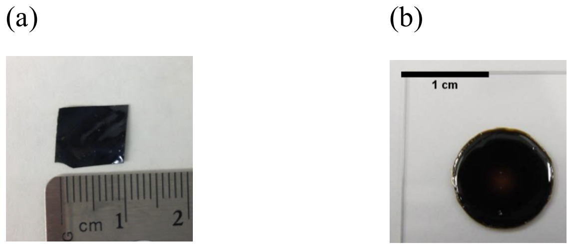
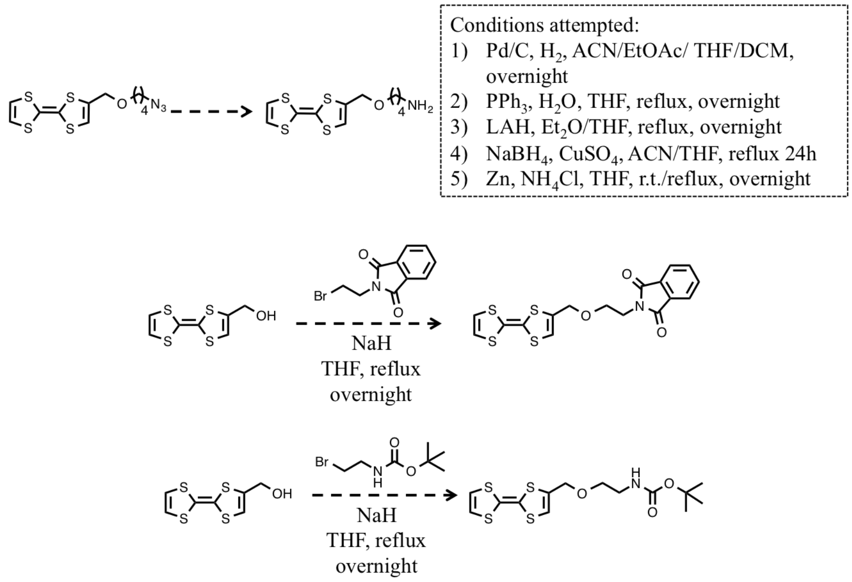


Figure S7. (a) Free-standing film of phmTTFMA; (b) phmTTFMA-chloranil film on glass substrate for electrical conductivity measurement.

IX. Attempted syntheses of TTF-derivatives with primary amine

Scheme S1. Attempted syntheses of TTF-derivatives with primary amine, where the starting materials were synthesized following literature reports.[1,2]



References:

(1) Tanaka, K.; Matsumoto, T.; Chujo, Y. *Synthetic Met.* **2013**, *163*, 13.

(2) Garín, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.; Wegener, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, *1994*, 489.