Supporting Information

Ferrocene-based Polyethyleneimines for Burning Rate Catalysts

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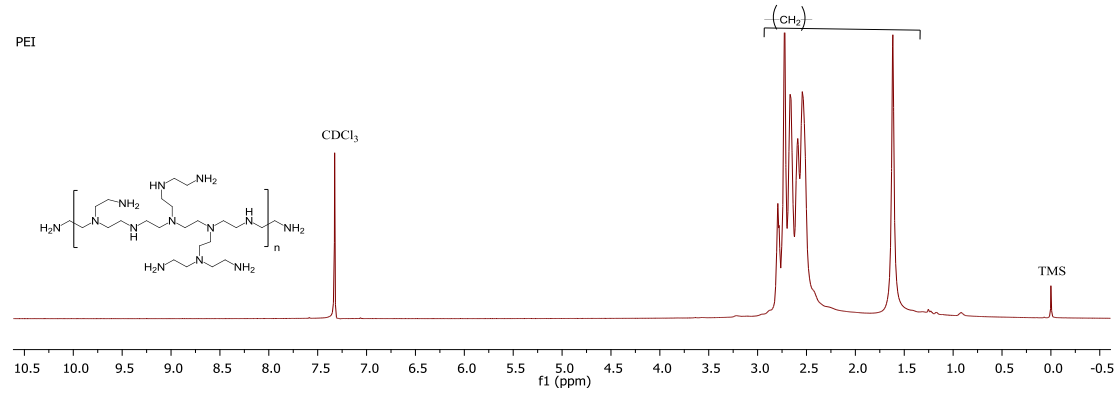
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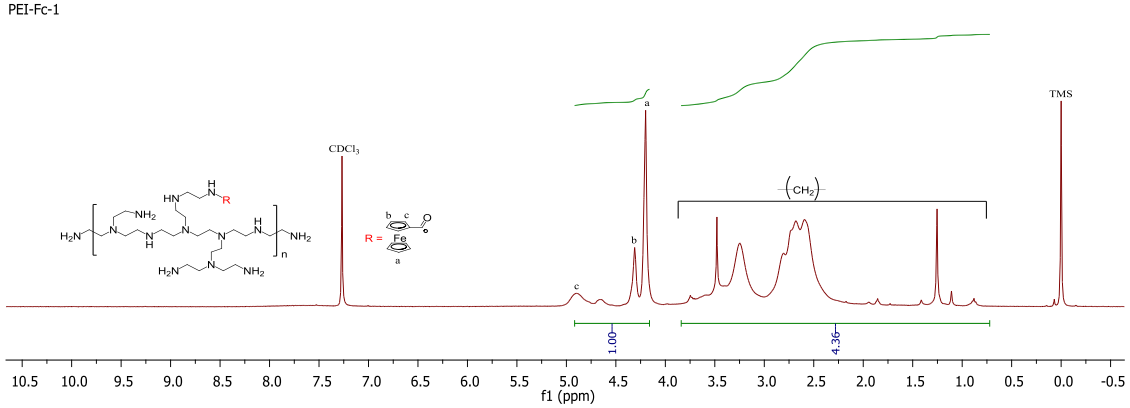
(CH2)
TMS
f1 (ppm)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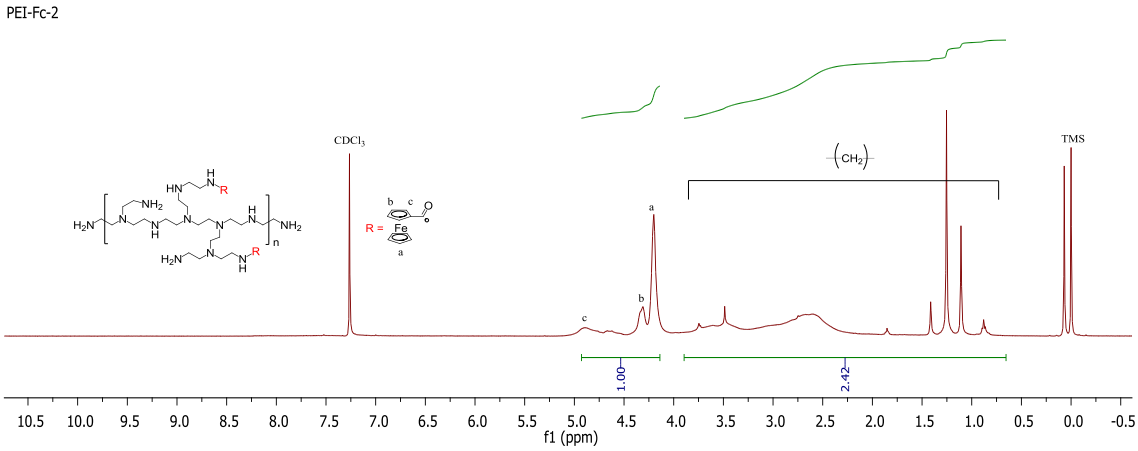
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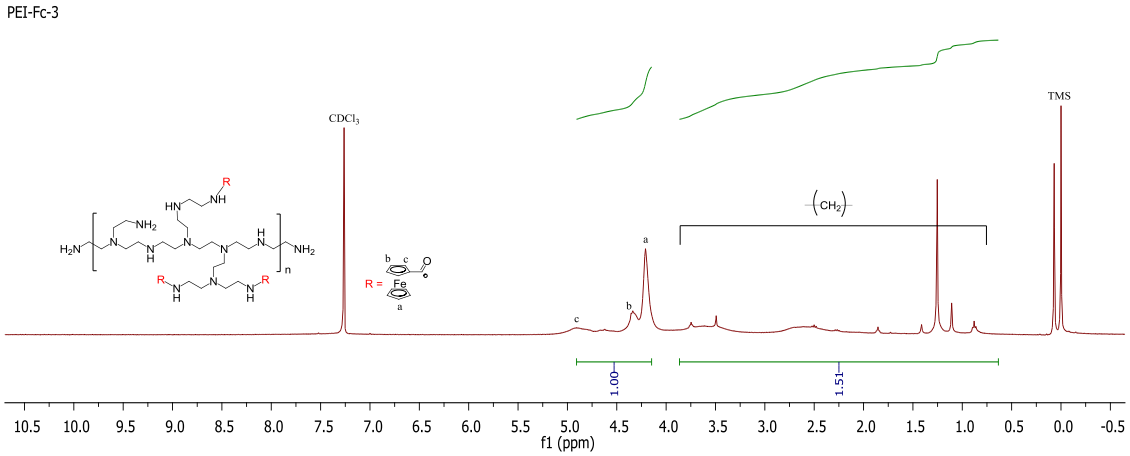
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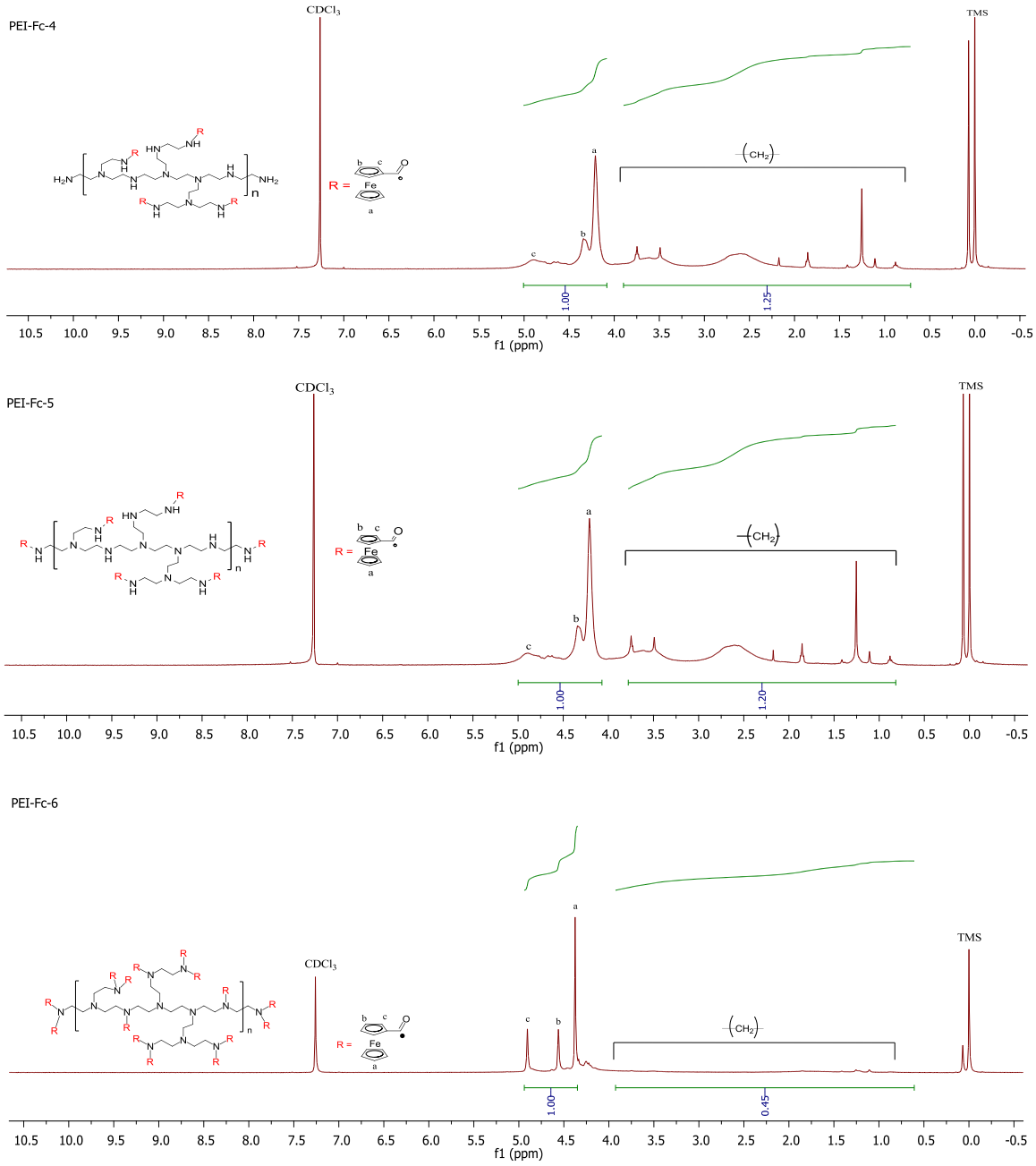

Figure S 1. ^{1}H NMR spectra of PEI, and PEI-Fcs.

Table S1. Experimental details for the synthesis of PEI-Fcs

Polymers	Polyethyleneimine, branched (A)			Ferrocenecarbonyl chloride (B)			Mole ratio	THF	TEA		Time	Temperature
	g	mmol	mol.L^{-1}	g	mmol	mol.L^{-1}	A : B	mL	mL	mmol	h	°C
PEI-Fc-1	4.65	11.16	0.12	2.77	11.16	0.12	1 : 1	90	1.6	11.74	18	25
PEI-Fc-2	2.11	5.06	0.07	2.51	10.12	0.14	1 : 2	70	1.5	10.75	18	25
PEI-Fc-3	1.55	3.72	0.04	2.77	11.16	0.12	1 : 3	90	1.6	11.74	18	25
PEI-Fc-4	1.16	2.79	0.03	2.77	11.16	0.12	1 : 4	90	1.6	11.74	18	25
PEI-Fc-5	0.93	2.23	0.02	2.77	11.16	0.12	1 : 5	90	1.6	11.74	18	25
PEI-Fc-6*	0.81	1.95	0.02	9.70	39.03	0.43	1 : 20	90	5.5	39.43	20	25

* After stirring at 25 °C, the reaction mixture was refluxed for 5 h.

Table S2. Relevant solvent parameters [22]

Solvent	DN	AN	ε	η	μ (D)
DMSO	29.8	19.3	46.6	2	3.96
DMF	26.6	16	36.7	0.82	3.8
THF	20	8	7.6	0.55	1.75
CH_2Cl_2	0	20.4	9.1	0.44	1.8
$CHCl_3$	0	23.1	4.8	0.57	1.1

"DN" and "AN" are the donor and the acceptor numbers of the solvents. "ε" is the dielectric constant at 25 °C, reflecting the degree of solvent polarity. "η" is the absolute viscosity at 25 °C, and "μ (D)" is the dipolar moment in Debye.

Table S3. Samples preparation for UV-Visible studies

Sample	Amount of the sample		Solvent	Total volume of solution	Concentration
	mg	mmol		mL	mmol/L
PEI-Fc-1	0.90	0.00125	DCM	25	0.05
PEI-Fc-2	1.10	0.00125	DCM	25	0.05
PEI-Fc-3	1.40	0.00125	DCM	25	0.05
PEI-Fc-4	1.70	0.00125	DCM	25	0.05
PEI-Fc-5	1.90	0.00125	DCM	25	0.05
PEI-Fc-6	3.50	0.00125	DCM	25	0.05

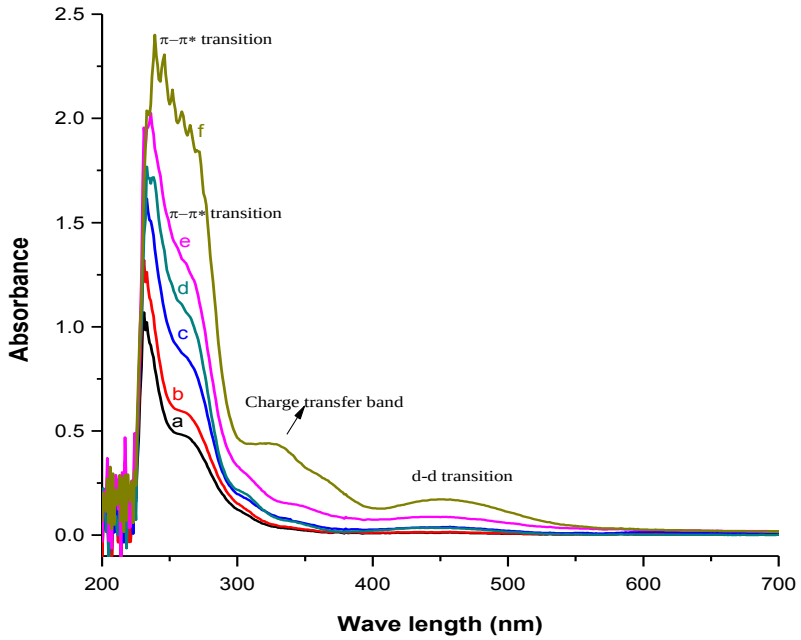

Figure S 2. UV-Vis spectra of PEI-Fcs: (a) PE-Fc-1, (b) PE-Fc-2, (c) PE-Fc-3, (d) PE-Fc-4, (e) PE-Fc-5 and (f) PE-Fc-6.

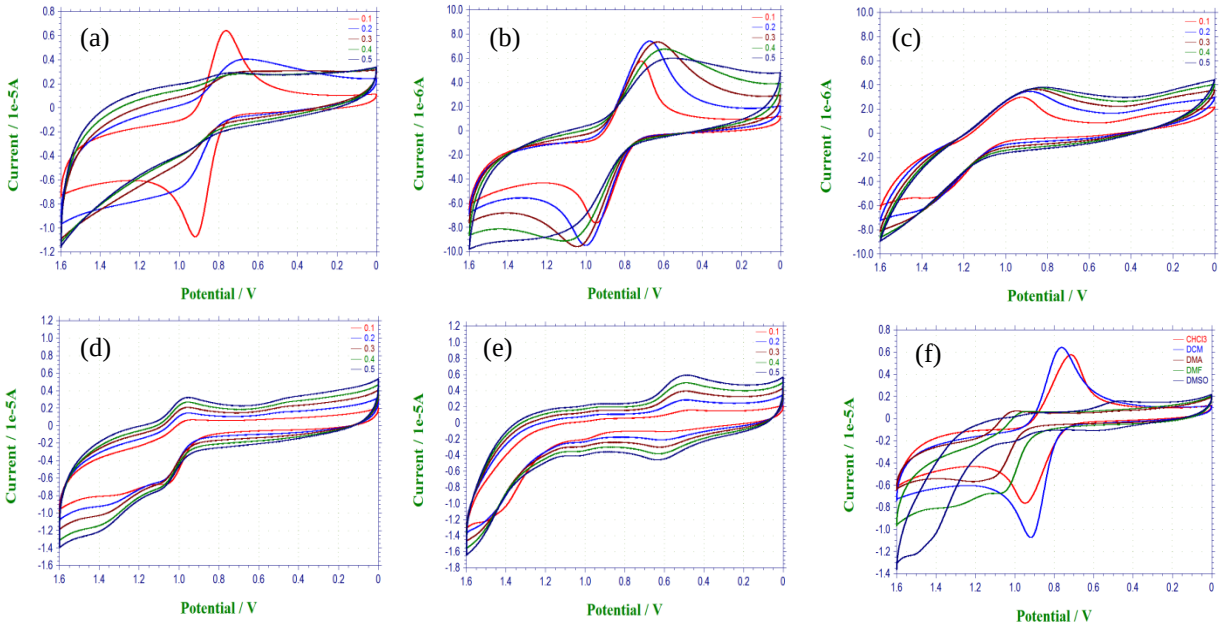

Figure S 3. CV curves of PEI-Fc-1 in: (a) DCM, (b) $CHCl_3$, (c) THF, (d) DMF, (e) DMSO at different scan rate (V/s), and (f) different organic solvents at 0.1 V/s

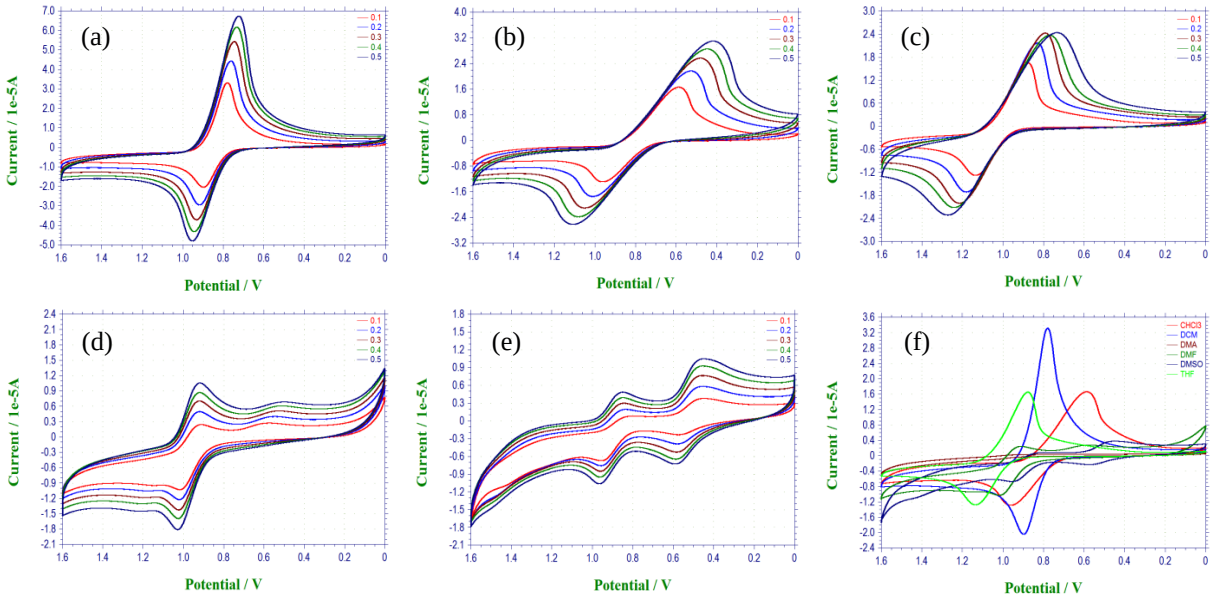

Figure S 4. CV curves of PEI-Fc-2 in: (a) DCM, (b) $CHCl_3$, (c) THF, (d) DMF, (e) DMSO at different scan rate (V/s), and (f) different organic solvents at 0.1 V/s

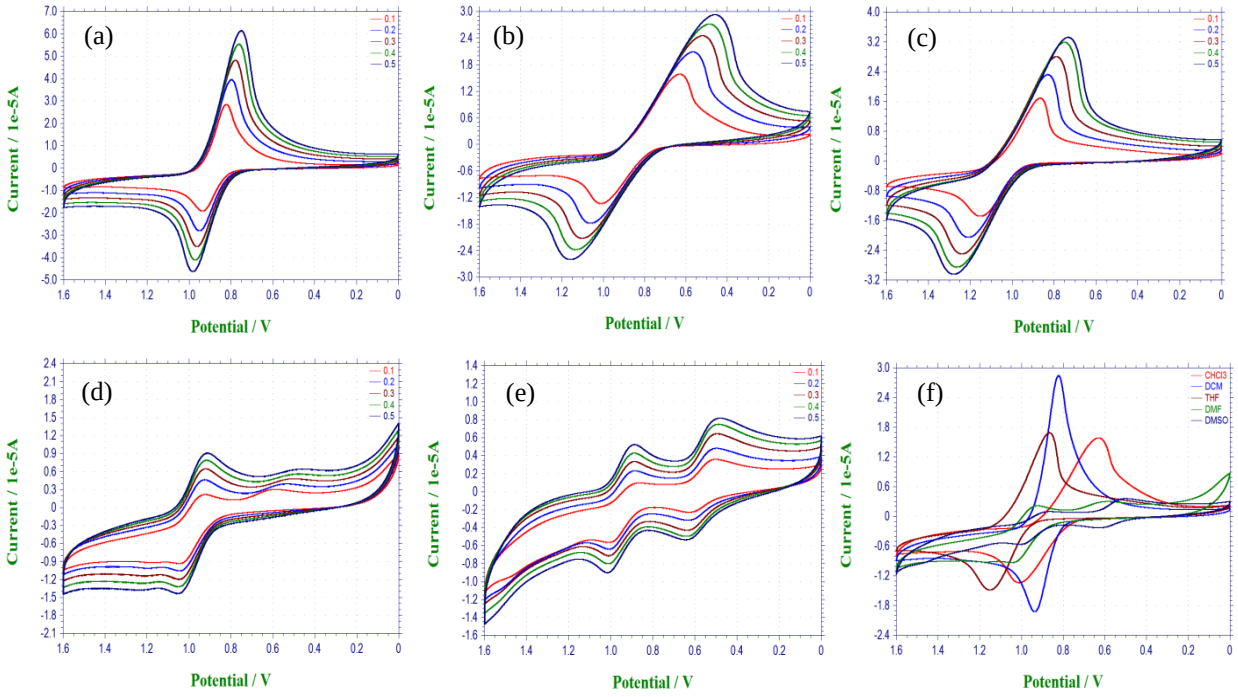

Figure S 5. CV curves of the PEI-Fc-3 in: (a) DCM, (b) $CHCl_3$, (c) THF, (d) DMF, (e) DMSO at different scan rate (V/s), and (f) different organic solvents at 0.1 V/s

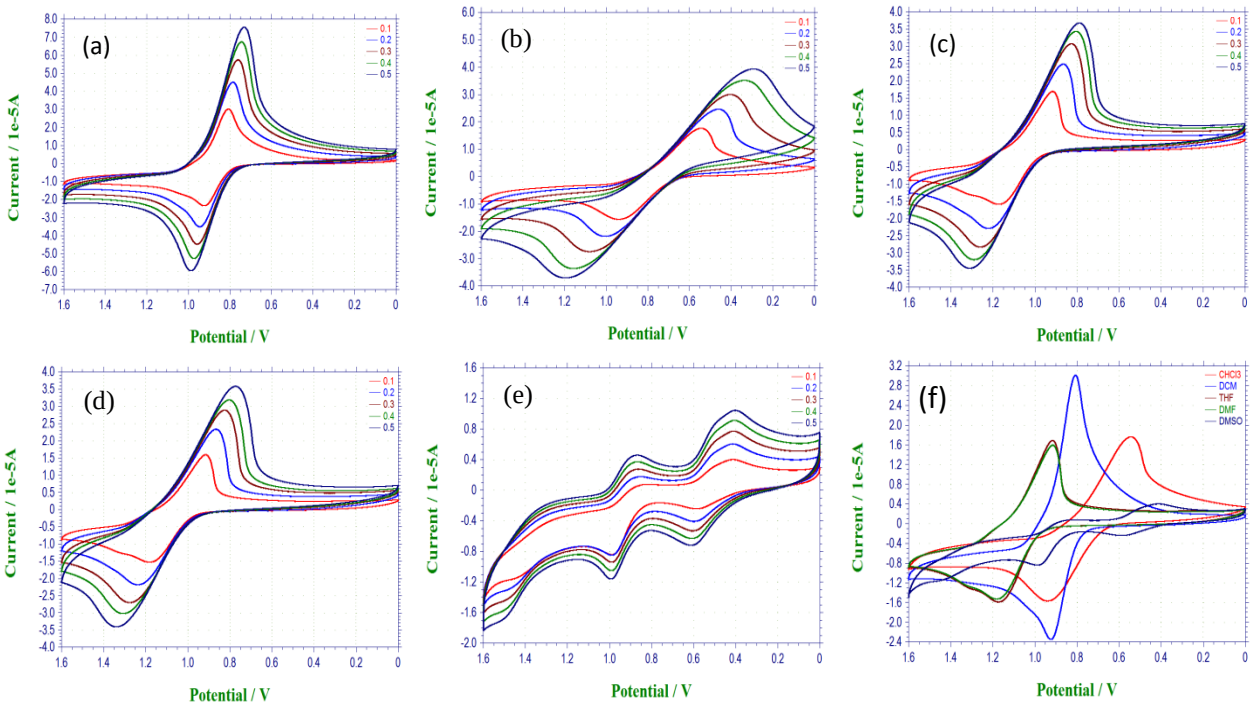

Figure S 6. CV curves of the PEI-Fc-4 in: (a) DCM, (b) $CHCl_3$, (c) THF, (d) DMF, (e) DMSO at different scan rate (V/s), and (f) different organic solvents at 0.1 V/s

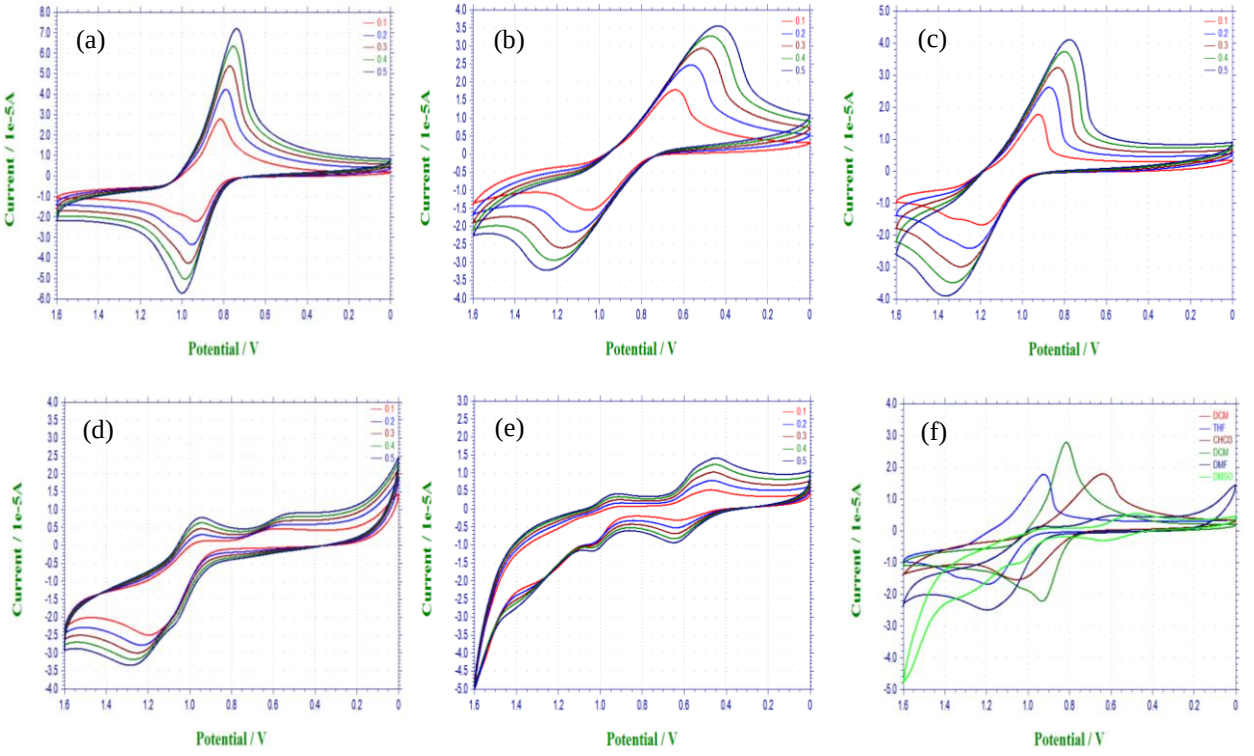

Figure S 7. CV curves of PEI-Fc-5 in: (a) DCM, (b) $CHCl_3$, (c) THF, (d) DMF, (e) DMSO at different scan rate (V/s), and (f) different organic solvents at 0.1 V/s

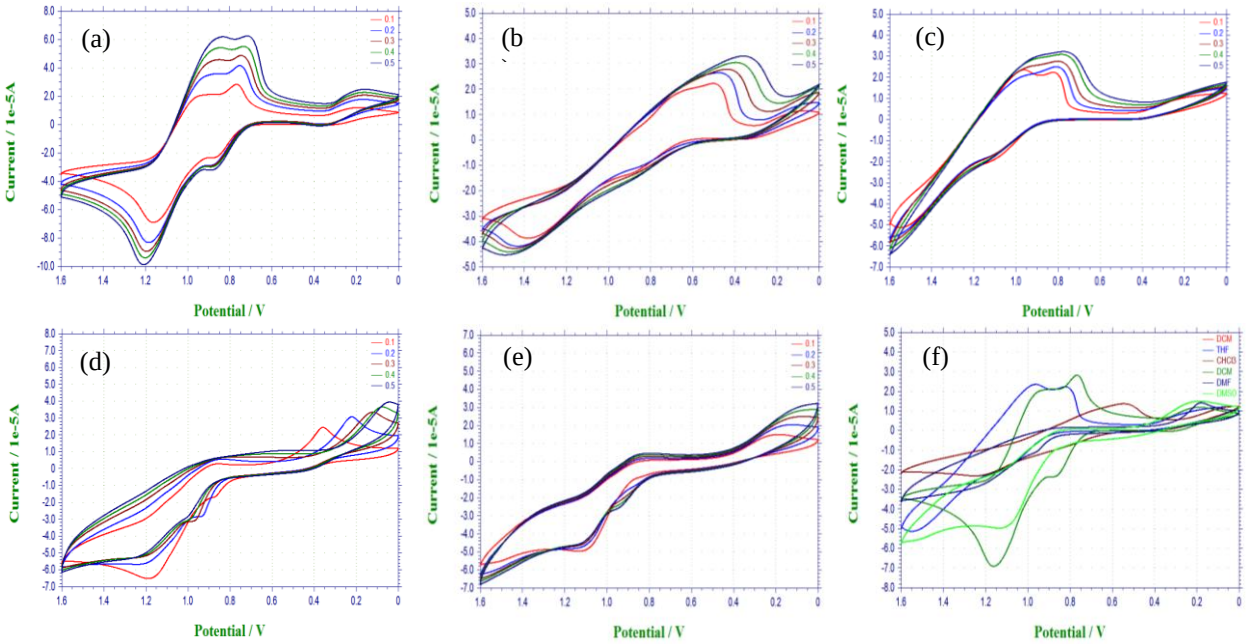

Figure S 8. CV curves of PEI-Fc-6 in: (a) DCM, (b) $CHCl_3$, (c) THF, (d) DMF, (e) DMSO at different scan rate (V/s), and (f) different organic solvents at 0.1 V/s

Table S4. Electrochemical data of PEI-Fcs in different organic solvents at 0.1 V/s

Polymer	Solvent	E_{PC} (V)	E_{PA} (V)	$^{a}E_P^{1/2}$ (V)	$^{b}\Delta E_P$ (V)	I_{PC} (μA)	I_{PA} (μA)	I_{PA}/I_{PC}
PEI-Fc-1	DCM	0.764	0.918	0.841	0.154	6.853	9.895	1.444
	$CHCl_3$	0.715	0.948	0.832	0.233	6.405	7.049	1.101
	THF	0.928	1.345	1.137	0.417	0.185	0.445	2.408
	DMF	0.972	1.057	1.015	0.085	0.839	5.300	6.315
	DMSO	0.468	0.566	0.517	0.098	0.864	0.345	0.399
PEI-Fc-2	DCM	0.779	0.897	0.838	0.118	3.486	1.949	0.559
	$CHCl_3$	0.589	0.961	0.775	0.372	18.080	12.250	0.678
	THF	0.878	1.135	1.007	0.257	1.791	1.215	0.678
	DMF	0.912	1.017	0.965	0.105	4.544	7.970	1.754
	DMSO	0.799	0.956	0.878	0.157	2.151	5.013	2.331
PEI-Fc-3	DCM	0.822	0.936	0.879	0.114	29.580	18.080	0.611
	$CHCl_3$	0.632	1.010	0.821	0.378	17.750	12.410	0.699
	THF	0.867	1.151	1.009	0.284	18.030	13.980	0.775
	DMF	0.924	1.049	0.987	0.125	4.220	6.514	1.544
	DMSO	0.860	1.008	0.934	0.148	1.949	3.893	1.997
PEI-Fc-4	DCM	0.807	0.923	0.865	0.116	33.680	21.920	0.651
	$CHCl_3$	0.545	0.938	0.742	0.393	19.180	14.770	0.770
	THF	0.916	1.171	1.044	0.255	9.119	14.710	1.613
	DMF	0.916	1.181	1.049	0.265	8.552	14.020	1.639
	DMSO	0.818	0.987	0.903	0.169	2.370	6.758	2.851

	DCM	0.816	0.933	0.875	0.117	31.560	20.660	0.655
	$CHCl_3$	0.643	1.050	0.847	0.407	17.200	14.610	0.849
PEI-Fc-5	**THF**	0.924	1.192	1.058	0.268	7.770	15.740	2.026
	DMF	0.964	1.194	1.079	0.230	6.673	22.740	3.408
	DMSO	0.475	0.630	0.553	0.155	3.539	2.028	0.573

[a]$E_P^{1/2} = (E_{PC} + E_{PA}) / 2$; [b]$\Delta E_P = E_{PA} - E_{PC}$

Table S5. Electrochemical data of PEI-Fc-1 at different scan rate in different organic solvents

Solvent	**Scan rate (V/s)**	E_{PC} **(V)**	E_{PA} **(V)**	$E_P^{1/2}$ **(V)**	ΔE_P **(V)**	I_{PC} **(μA)**	I_{PA} **(μA)**	I_{PA}/I_{PC}
DCM	0.1	0.764	0.918	0.841	0.154	6.853	9.895	1.444
	0.2	0.698	1.035	0.866	0.337	2.519	5.575	2.213
	0.3	0.725	0.977	0.851	0.252	0.914	2.547	2.787
	0.4	0.733	0.964	0.848	0.231	0.373	1.521	4.078
	0.5	0.761	0.997	0.879	0.236	0.463	1.414	3.052
$CHCl_3$	0.1	0.715	0.948	0.832	0.233	6.405	7.049	1.101
	0.2	0.674	0.999	0.837	0.325	7.555	8.604	1.139
	0.3	0.639	1.039	0.839	0.400	6.472	8.325	1.286
	0.4	0.616	1.093	0.855	0.477	5.091	7.313	1.436
	0.5	0.603	1.202	0.903	0.599	3.937	6.357	1.615
THF	0.1	0.928	1.345	1.137	0.417	0.185	0.445	2.408
	0.2	0.884	1.404	1.144	0.520	1.118	5.078	4.542
	0.3	0.865	-	-	-	0.068	-	-
	0.4	0.837	-	-	-	0.048	-	-
	0.5	0.855	-	-	-	0.038	-	-
DMF	0.1	0.972	1.057	1.015	0.085	0.839	5.300	6.315
	0.2	0.975	1.087	1.031	0.112	1.371	4.594	3.351
	0.3	0.975	1.085	1.030	0.110	1.745	4.249	2.435
	0.4	0.968	1.094	1.031	0.126	2.040	4.304	2.110
	0.5	0.970	1.103	1.037	0.133	2.099	4.232	2.016
DMSO	0.1	0.468	0.566	0.517	0.098	0.864	0.345	0.399
	0.2	0.489	0.569	0.529	0.080	1.691	0.260	0.154
	0.3	0.494	0.595	0.545	0.101	2.198	0.593	0.270
	0.4	0.489	0.603	0.546	0.114	2.721	0.660	0.242
	0.5	0.486	0.610	0.548	0.124	3.463	1.235	0.357

Table S6. Electrochemical data of PEI-Fc-2 at different scan rate in different organic solvents

Solvent	Scan rate (V/s)	E_{PC} (V)	E_{PA} (V)	$E_P^{1/2}$ (V)	ΔE_P (V)	I_{PC} (μA)	I_{PA} (μA)	I_{PA}/I_{PC}
DCM	0.1	0.779	0.897	0.838	0.118	3.486	1.949	0.559
	0.2	0.761	0.916	0.839	0.155	4.556	2.823	0.620
	0.3	0.744	0.930	0.837	0.186	5.674	35.320	6.225
	0.4	0.734	0.941	0.838	0.207	63.870	41.143	0.644
	0.5	0.724	0.952	0.838	0.228	6.865	4.609	0.671
$CHCl_3$	0.1	0.589	0.961	0.775	0.372	18.080	12.250	0.678
	0.2	0.529	1.008	0.769	0.479	22.640	16.340	0.722
	0.3	0.479	1.048	0.764	0.569	27.310	19.460	0.713
	0.4	0.447	1.077	0.762	0.630	29.920	21.790	0.728
	0.5	0.418	1.106	0.762	0.688	31.550	23.600	0.748
THF	0.1	0.878	1.135	1.007	0.257	1.791	1.215	0.678
	0.2	0.833	1.181	1.007	0.348	2.252	1.600	0.710
	0.3	0.796	1.212	1.004	0.416	2.406	1.880	0.781
	0.4	0.774	1.244	1.009	0.470	2.285	1.971	0.863
	0.5	0.743	1.272	1.008	0.529	2.256	2.120	0.940
DMF	0.1	0.912	1.017	0.965	0.105	4.544	7.970	1.754
	0.2	0.921	1.019	0.970	0.098	6.393	10.400	1.627
	0.3	0.922	1.025	0.974	0.103	7.973	9.052	1.135
	0.4	0.922	1.026	0.974	0.104	9.168	11.540	1.259
	0.5	0.917	1.028	0.973	0.111	10.790	13.260	1.229
DMSO	0.1	0.799	0.956	0.878	0.157	2.151	5.013	2.331
	0.2	0.833	0.956	0.895	0.123	2.935	4.845	1.651
	0.3	0.846	0.958	0.902	0.112	3.449	4.830	1.400
	0.4	0.849	0.962	0.906	0.113	3.887	4.992	1.284
	0.5	0.850	0.964	0.907	0.114	4.465	5.476	1.226

Table S7. Electrochemical data of PEI-Fc-3 at different scan rate in different organic solvents

Solvent	Scan rate (V/s)	E_{PC} (V)	E_{PA} (V)	$E_P^{1/2}$ (V)	ΔE_P (V)	I_{PC} (μA)	I_{PA} (μA)	I_{PA}/I_{PC}
DCM	0.1	0.822	0.936	0.879	0.114	29.580	18.080	0.611
	0.2	0.799	0.951	0.875	0.152	40.900	25.910	0.633
	0.3	0.778	0.961	0.870	0.183	49.110	31.740	0.646
	0.4	0.762	0.971	0.867	0.209	56.370	39.040	0.693
	0.5	0.752	0.981	0.867	0.229	62.330	43.960	0.705
$CHCl_3$	0.1	0.632	1.010	0.821	0.378	17.750	12.410	0.699
	0.2	0.569	1.061	0.815	0.492	22.680	16.590	0.731
	0.3	0.521	1.102	0.812	0.581	25.920	19.630	0.757
	0.4	0.492	1.129	0.811	0.637	28.300	21.760	0.769
	0.5	0.464	1.153	0.809	0.689	13.100	23.160	1.768

	0.1	0.867	1.151	1.009	0.284	18.030	13.980	0.775
	0.2	0.833	1.207	1.020	0.374	23.660	19.130	0.809
THF	0.3	0.791	1.240	1.016	0.449	28.300	23.210	0.820
	0.4	0.752	1.260	1.006	0.508	31.900	26.340	0.826
	0.5	0.739	1.276	1.008	0.537	31.790	28.420	0.894
	0.1	0.924	1.049	0.987	0.125	4.220	6.514	1.544
	0.2	0.926	1.047	0.987	0.121	5.709	7.340	1.286
DMF	0.3	0.919	1.046	0.983	0.127	6.829	8.320	1.218
	0.4	0.918	1.053	0.986	0.135	7.720	9.049	1.172
	0.5	0.922	1.052	0.987	0.130	8.580	9.932	1.158
	0.1	0.860	1.008	0.934	0.148	1.949	3.893	1.997
	0.2	0.885	1.007	0.946	0.122	2.868	3.980	1.388
DMSO	0.3	0.892	1.007	0.950	0.115	3.283	3.806	1.159
	0.4	0.888	1.011	0.950	0.123	3.806	4.119	1.082
	0.5	0.888	1.016	0.952	0.128	4.455	4.698	1.055

Table S8. Electrochemical data of PEI-Fc-4 at different scan rate in different organic solvents

Solvent	**Scan rate (V/s)**	E_{PC} **(V)**	E_{PA} **(V)**	$E_P^{1/2}$ **(V)**	ΔE_P **(V)**	I_{PC} **(μA)**	I_{PA} **(μA)**	I_{PA}/I_{PC}
	0.1	0.807	0.923	0.865	0.116	33.680	21.920	0.651
	0.2	0.785	0.945	0.865	0.160	48.190	33.170	0.688
DCM	0.3	0.760	0.958	0.859	0.198	60.040	12.480	0.208
	0.4	0.744	0.973	0.859	0.229	68.460	50.110	0.732
	0.5	0.731	0.987	0.859	0.256	77.720	56.300	0.724
	0.1	0.545	0.938	0.742	0.393	19.180	14.770	0.770
	0.2	0.465	0.997	0.731	0.532	26.340	20.140	0.765
$CHCl_3$	0.3	0.407	1.066	0.737	0.659	31.190	25.290	0.811
	0.4	0.348	1.143	0.746	0.795	35.920	29.160	0.812
	0.5	0.306	1.169	0.738	0.863	39.000	30.340	0.778
	0.1	0.916	1.171	1.044	0.255	9.119	14.710	1.613
	0.2	0.866	1.221	1.044	0.355	8.546	21.160	2.476
THF	0.3	0.845	1.257	1.051	0.412	14.210	26.340	1.854
	0.4	0.798	1.284	1.041	0.486	14.170	29.270	2.066
	0.5	0.781	1.311	1.046	0.530	16.800	31.820	1.894
	0.1	0.916	1.181	1.049	0.265	8.552	14.020	1.639
	0.2	0.866	1.234	1.050	0.368	7.047	20.010	2.840
DMF	0.3	0.816	1.276	1.046	0.460	12.700	25.170	1.982
	0.4	0.796	1.306	1.051	0.510	12.540	27.240	2.172
	0.5	0.764	1.339	1.052	0.575	15.640	31.560	2.018
	0.1	0.818	0.987	0.903	0.169	2.370	6.758	2.851
DMSO	0.2	0.852	0.991	0.922	0.139	2.972	5.680	1.911
	0.3	0.861	0.990	0.926	0.129	3.539	5.703	1.611

	0.4	0.866	0.989	0.928	0.123	4.127	5.989	1.451
	0.5	0.872	0.990	0.931	0.118	4.656	6.308	1.355

Table S9. Electrochemical data of PEI-Fc-5 at different scan rate in different organic solvents

Solvent	Scan rate (V/s)	E_{PC} (V)	E_{PA} (V)	$E_P^{1/2}$ (V)	ΔE_P (V)	I_{PC} (μA)	I_{PA} (μA)	I_{PA}/I_{PC}
DCM	0.1	0.816	0.933	0.875	0.117	31.560	20.660	0.655
	0.2	0.791	0.952	0.872	0.161	65.120	31.800	0.488
	0.3	0.771	0.970	0.871	0.199	56.780	40.520	0.714
	0.4	0.755	0.985	0.870	0.230	45.020	48.050	1.067
	0.5	0.739	0.998	0.869	0.259	73.710	54.460	0.739
$CHCl_3$	0.1	0.643	1.050	0.847	0.407	17.200	14.610	0.849
	0.2	0.570	1.119	0.845	0.549	22.940	20.080	0.875
	0.3	0.522	1.167	0.845	0.645	28.260	24.000	0.849
	0.4	0.483	1.208	0.846	0.725	29.450	26.290	0.893
	0.5	0.446	0.239	0.343	-0.207	32.440	28.840	0.889
THF	0.1	0.924	1.192	1.058	0.268	7.770	15.740	2.026
	0.2	0.872	1.246	1.059	0.374	6.691	22.450	3.355
	0.3	0.829	1.288	1.059	0.459	11.050	27.870	2.522
	0.4	0.803	1.328	1.066	0.525	12.940	32.130	2.483
	0.5	0.772	1.361	1.066	0.589	14.130	35.890	2.540
DMF	0.1	0.964	1.194	1.079	0.230	6.673	22.740	3.408
	0.2	0.965	1.229	1.097	0.264	7.073	23.830	3.369
	0.3	0.945	1.241	1.093	0.296	4.941	23.810	4.819
	0.4	0.946	1.257	1.102	0.311	6.074	24.080	3.964
	0.5	0.944	1.270	1.107	0.326	6.993	24.570	3.514
DMSO	0.1	0.475	0.630	0.553	0.155	3.539	2.028	0.573
	0.2	0.466	0.639	0.553	0.173	6.333	3.237	0.511
	0.3	0.463	0.643	0.553	0.180	7.665	4.039	0.527
	0.4	0.452	0.649	0.551	0.197	9.292	4.672	0.503
	0.5	0.448	0.645	0.547	0.197	10.540	5.146	0.488

Table S10. Samples preparation for CV studies

Sample	Amount of the sample			Amount of electrolyte (Bu_4NBF_4)			*Total volume of the solution
	mg	mmol	mmol/L	mg	mmol	mmol/L	mL
PEI-Fc-1	3.43	0.005	0.50	329.27	1.00	100	10
PEI-Fc-2	4.49	0.005	0.50	329.27	1.00	100	10
PEI-Fc-3	5.60	0.005	0.50	329.27	1.00	100	10
PEI-Fc-4	6.20	0.005	0.50	329.27	1.00	100	10
PEI-Fc-5	6.61	0.005	0.50	329.27	1.00	100	10
PEI-Fc-6	12.80	0.005	0.50	329.27	1.00	100	10

Ferrocene	2.00	0.005	0.50	329.27	1.00	100	10

***Solvents used for the preparation of solution were DCM, $CHCl_3$, THF, DMF and DMSO, respectively.**

Table S11. Samples preparation for migration studies

Sample	Ammonium perchlorate (AP)		BRC		Hydroxyterminated polybutadiene (HTPB)		Isophorone diisocyanate	
	g	Wt. %	g	Wt. %	g	Wt. %	g	Wt. %
Blank	7.0535	71.93	-	-	2.0873	21.28	0.6657	6.79
Ferrocene	1.9183	70.63	0.0814	3.00	0.5461	20.10	0.1701	6.26
Catocene	1.9152	70.34	0.0899	3.30	0.5465	20.07	0.1711	6.28
PEI-Fc-1	1.9185	70.69	0.0817	3.01	0.5438	20.04	0.1699	6.26
PEI-Fc-4	1.9194	70.62	0.0818	3.01	0.5474	20.14	0.1693	6.23
PEI-Fc-6	1.9162	70.66	0.0815	3.00	0.5443	20.07	0.1699	6.26

Table S12. Samples preparation for TG and DTG analysis

Sample No.	Sample Code	Amount of PEI-Fcs (mg)	Amount of AP (mg)	Total amount (mg)	Wt.% of the PEI-Fcs	Amount of the sample used (mg)
1	AP	-	3.0	3.0	-	3.0
2	AP + 5 Wt.% of PEI-Fc-1	2.0	38.0	40	5	2.95
3	AP + 5 Wt.% of PEI-Fc-2	2.0	38.0	40	5	2.80
4	AP + 5 Wt.% of PEI-Fc-3	2.0	38.0	40	5	2.85
5	AP + 5 Wt.% of PEI-Fc-4	2.0	38.0	40	5	3.00
6	AP + 5 Wt.% of PEI-Fc-5	2.0	38.0	40	5	2.69
7	AP + 5 Wt.% of PEI-Fc-6	2.0	38.0	40	5	2.95
8	AP + 1 Wt.% of PEI-Fc-6	0.5	49.5	50	1	2.70
9	AP + 2 Wt.% of PEI-Fc-6	0.6	29.4	30	2	2.83
10	AP + 3 Wt.% of PEI-Fc-6	0.9	29.1	30	3	2.84
11	AP + 4 Wt.% of PEI-Fc-6	1.2	28.8	30	4	2.85
12	AP + 5 Wt.% of PEI-Fc-6	2.0	38.0	40	5	2.97

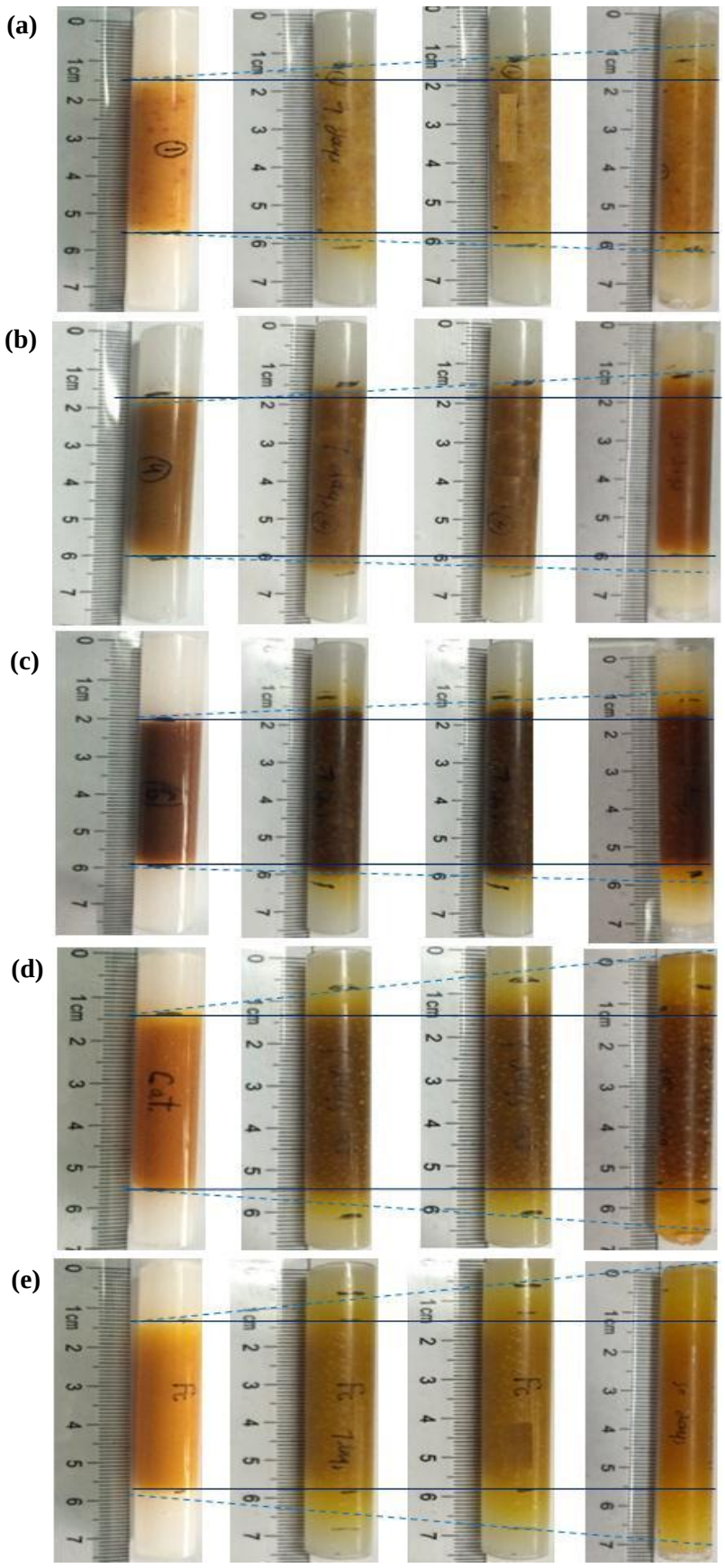

Figure S 9. Migration photos of: (a) PEI-Fc-1, (b) PEI-Fc-4, (c) PEI-Fc-6, (d) catocene and (e) ferrocene on first day, 7 days, 15 days, and 30 days at 50 °C.