Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Molecular design of ionic liquids as novel nonmetallic catalysts used in acetylene hydrochlorination reaction

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Table S1a. IR Spectra of TPPB

Calculations (v/cm^{-1})	**Experiments (v/cm^{-1})**	**Assignments[1-5]**
528	521	σ C-P
677	690	γ C-H
709	718	w C-C
741	745	γ C-H
768	761	vas C-P
982	991	ring breathing
1071	1099	r C-H
1422	1437	σ C-H
1517	1477	σ C-H
1571	1578	v C=C
2924		v C-H
3094	3036	v C-H

Noted: Frequency was calculated at B3LYP/6-311G(d,p) and frequency correction factor was set as 0.9682[6].

Table S1b. IR Spectra of TPPC

Calculations (ν/cm^{-1})	**Experiments (ν/cm^{-1})**	**Assignments[1-5]**
528	528	σ C-P
677	692	γ C-H
709	723	w C-C
741	754	γ C-H
986	997	ring breathing
1071	1107	r C-H
1320	1313	r C-H
1422	1439	σ C-H
1571	1583	v C=C
	2854	v C-H
2903		v C-H
	2954	v C-H
3094	3064	v C-H

Table S1c. IR Spectra of BuTPPB

Calculations (ν/cm^{-1})	**Experiments (ν/cm^{-1})**	**Assignments[1-5]**
496	494	σ C-P
528	532	σ C-P
687	690	γ C-H
709	721	w C-C
730	744	γ C-H
773	758	vas C-P
	806	r C-H
1071	1093	r C-H
1422	1437	σ C-H
2881	2865	v C-H
2903	2885	v C-H
2956	2958	v C-H
2999	3004	v C-H
	3051	v C-H
3094	3074	v C-H

Table S1d. IR Spectra of TPPT

Calculations (ν/cm^{-1})	Experiments (ν/cm^{-1})	Assignments[1-5]
517	528	σ C-P
687	691	σ C-P, v BF_4
709	724	w C-C
741	750	γ C-H, v BF_4
932	916	γ C-H, v BF_4
1007	999	ring breathing
1081	1069	r C-H
1124	1125	r C-H, v BF_4
1177	1195	r C-H
1422	1436	σ C-H
1571		v C=C
3094	3105	v C-H
3235	3265	v C-H

Table S2a. Mulliken charge changes in the adsorption configuration

Configuration	Group	TPPB	TPPC	BuTPPB	TPPT
Adsorption of HCl	HCl	-0.188	-0.210	-0.185	-0.079
	IL anion	0.110	0.128	0.118	0.047
	IL cation	0.078	0.082	0.067	0.032
Adsorption of C_2H_2	C_2H_2	-0.037	-0.025	-0.043	-0.038
	IL anion	0.020	0.014	0.027	0.037
	IL cation	0.017	0.011	0.016	0.001
Adsorption of C_2H_3Cl	C_2H_3Cl	-0.040	-0.021	-0.039	-0.049
	IL anion	0.010	-0.028	0.012	0.032
	IL cation	0.030	0.049	0.027	0.017

Note: Positive value means losing electrons; Negative value means getting electrons.

Table S2b. NPA charge changes in the adsorption configuration

Configuration	Group	TPPB	TPPC	BuTPPB	TPPT
Adsorption of HCl	HCl	-0.187	-0.221	-0.179	-0.052
	IL anion	0.131	0.164	0.133	0.041
	IL cation	0.056	0.057	0.046	0.011
Adsorption of C_2H_2	C_2H_2	-0.026	-0.026	-0.026	-0.017
	IL anion	-0.002	0.002	0.005	0.013
	IL cation	0.028	0.024	0.021	0.004
Adsorption of C_2H_3Cl	C_2H_3Cl	-0.011	-0.012	-0.012	-0.009
	IL anion	-0.013	-0.009	-0.005	0.004
	IL cation	0.024	0.021	0.017	0.005

Table S2c. Hirshfeld charge changes in the adsorption configuration

Configuration	Group	TPPB	TPPC	BuTPPB	TPPT
Adsorption of HCl	HCl	-0.233	-0.264	-0.221	-0.101
	IL anion	0.158	0.185	0.168	0.096
	IL cation	0.065	0.079	0.053	0.005
Adsorption of C_2H_2	C_2H_2	-0.076	-0.085	-0.083	-0.046
	IL anion	0.048	0.060	0.060	0.056
	IL cation	0.028	0.025	0.023	-0.010
Adsorption of C_2H_3Cl	C_2H_3Cl	-0.044	-0.056	-0.046	-0.031
	IL anion	0.034	0.048	0.045	0.041
	IL cation	0.010	0.008	0.001	-0.010

Table S3. Relative energies during reaction processes and reaction activation energies

Structure Energy (kJ/mol)	Co-ads	IM	TS	Pr-ads	Pr	Energy Barrier	Activation Energy (ΔG_{453})
TPPB	0	58.85	118.59	-47.99	-30.89	59.73	85.65
TPPC	0	47.44	115.91	-41.93	-23.78	68.47	92.13
BuTPPB	0	31.27	119.13	-49.37	-32.52	87.86	118.67
TPPT	0	14.04	156.37	-72.40	-47.65	142.33	157.75
Without catalyst	0		178.49		-101.57	178.49	189.56

Table S4. The catalytic performance of non-metal catalyst for acetylene hydrochlorination recently reported in literatures.

Catalyst	Reaction conditions	Initial maximum C_2H_2 conversion
SiC@N-C[7]	T= 473 K. $GHSV$ (C_2H_2) = 30 h^{-1}. V_{HCl}/V_{C2H2}= 1.15	80.0%
g-C3N4/AC[8]	T= 453 K. $GHSV$ (C_2H_2) = 50 h^{-1}. V_{HCl}/V_{C2H2}= 0.85	75.0%
N-OMC-700[9]	T= 473 K. $GHSV$ (C_2H_2) = 32 h^{-1}. V_{HCl}/V_{C2H2}= 1.15	77.0%
PANI-AC900[10]	T= 453 K. $GHSV$ (C_2H_2) = 36 h^{-1}. V_{HCl}/V_{C2H2}= 1.15	76.0%
Z4M1[11]	T= 453 K. $GHSV$ (C_2H_2) = 50 h^{-1}. V_{HCl}/V_{C2H2}= 1.15	60.0%
N-OMC-O2.0[12]	T= 180 K. $GHSV$ (C_2H_2) = 50 h^{-1}. V_{HCl}/V_{C2H2}= 1.1	34.0%
AC-n-U500[13]	T= 483 K. $GHSV$ (C_2H_2) = 50 h^{-1}. V_{HCl}/V_{C2H2}= 1.2	81.0%
ZIF-8/SAC[14]	T= 220 K. $GHSV$ (C_2H_2) = 30 h^{-1}. V_{HCl}/V_{C2H2}= 1.15	81.0%
PDA/SiC-700[15]	T= 493 K. $GHSV$ (C_2H_2) = 0.08ml g^{-1} min^{-1}. V_{HCl}/V_{C2H2}= 1.15	77%
NS-C-NH_3[16]	T= 493 K. $GHSV$ (C_2H_2) = 35 h^{-1}. V_{HCl}/V_{C2H2}= 1.2	80%
p-BN[17]	T= 553 K. $GHSV$ (C_2H_2) = 1.32 mL min^{-1} g^{-1}. V_{HCl}/V_{C2H2}= 1.2	99 %
15%TPPB/SAC[this work]	T= 453 K. $GHSV$ (C_2H_2) = 50 h^{-1}. V_{HCl}/V_{C2H2}= 1.15	84.0%

Note: The reaction temperature has a great influence on the C_2H_2 conversion in acetylene hydrochlorination. The higher reaction temperature is, the higher C_2H_2 conversion achieved.

Table S5a. Mulliken charge changes during acetylene hydrochlorination reaction

Catalyst	Group/ atom	ΔCharge (Co ads-free)	ΔCharge (IM-Co ads)	ΔCharge (TS-IM)	ΔCharge (Pr-TS)
TPPB catalyst	H2	0.043	-0.050	0.058	-0.053
	C1	0.029	-0.144	-0.013	0.093
	C2	-0.080	0.157	0.059	-0.245
	H3	-0.014	0.057	0.062	-0.067
	C_2H_2	-0.022	0.020	0.166	-0.272
	Cl1	-0.195	-0.431	0.044	0.638
	H1	0.028	-0.050	0.074	-0.038
	HCl	-0.167	-0.481	0.118	0.600
	IL anion	0.102	0.483	-0.330	-0.245
	IL cation	0.087	-0.022	0.046	-0.083
	IL	0.189	0.461	-0.284	-0.328
TPPC catalyst	H2	0.062	-0.067	0.049	-0.052
	C1	0.031	-0.149	-0.040	0.116
	C2	-0.083	0.159	0.046	-0.229
	H3	-0.014	0.056	0.050	-0.056
	C_2H_2	-0.004	-0.001	0.105	-0.221
	Cl1	-0.229	-0.392	0.045	0.626
	H1	0.060	-0.022	0.073	-0.062
	HCl	-0.169	-0.414	0.118	0.564
	IL anion	0.085	0.461	-0.291	-0.283
	IL cation	0.088	-0.046	0.068	-0.060
	IL	0.173	0.415	-0.223	-0.343

BuTPPB catalyst	H2	0.044	-0.052	0.057	-0.051
	C1	0.035	-0.144	-0.025	0.098
	C2	-0.092	0.144	0.080	-0.242
	H3	-0.014	0.115	0.007	-0.070
	C_2H_2	-0.027	0.063	0.119	-0.265
	Cl1	-0.183	-0.488	0.073	0.655
	H1	0.028	-0.051	0.075	-0.038
	HCl	-0.155	-0.539	0.148	0.617
	IL anion	0.114	0.473	-0.316	-0.259
	IL cation	0.068	0.003	0.049	-0.093
	IL	0.182	0.476	-0.267	-0.352
TPPT catalyst	H2	0.055	0.014	0.063	-0.108
	C1	0.024	0.014	-0.048	-0.054
	C2	-0.098	-0.008	0.242	-0.229
	H3	-0.015	0.003	0.094	-0.040
	C_2H_2	-0.034	0.023	0.351	-0.431
	Cl1	-0.141	0.051	-0.412	0.551
	H1	0.068	-0.037	0.044	-0.082
	HCl	-0.073	0.014	-0.368	0.469
	IL anion	0.070	-0.034	0.014	-0.019
	IL cation	0.037	-0.003	0.003	-0.019
	IL	0.107	-0.037	0.017	-0.038

Table S5b. NPA charge changes during acetylene hydrochlorination reaction

Catalyst	Group/ atom	ΔCharge (Co ads-free)	ΔCharge (IM-Co ads)	ΔCharge (TS-IM)	ΔCharge (Pr-TS)
TPPB catalyst	H2	0.034	-0.031	0.045	-0.068
	C1	0.006	-0.093	-0.189	0.125
	C2	-0.052	0.083	0.290	-0.307
	H3	-0.006	0.056	-0.004	-0.078
	C_2H_2	-0.018	0.014	0.143	-0.328
	Cl1	-0.172	-0.466	0.106	0.720
	H1	0.008	-0.035	0.036	-0.019
	HCl	-0.165	-0.501	0.142	0.701
	IL anion	0.117	0.506	-0.309	-0.326
	IL cation	0.065	-0.019	0.024	-0.047
	IL	0.183	0.487	-0.285	-0.373
TPPC catalyst	H2	0.039	-0.035	0.037	-0.065
	C1	0.009	-0.097	-0.176	0.113
	C2	-0.058	0.084	0.254	-0.266
	H3	-0.006	0.057	-0.016	-0.069
	C_2H_2	-0.016	0.009	0.099	-0.286
	Cl1	-0.208	-0.428	0.113	0.710
	H1	0.012	0.025	-0.013	-0.028
	HCl	-0.196	-0.403	0.100	0.681
	IL anion	0.149	0.422	-0.224	-0.355
	IL cation	0.064	-0.028	0.025	-0.040
	IL	0.212	0.394	-0.199	-0.395

BuTPPB catalyst	H2	0.033	-0.031	0.044	-0.066
	C1	0.014	-0.088	-0.199	0.122
	C2	-0.056	0.084	0.282	-0.296
	H3	-0.006	0.056	-0.002	-0.080
	C_2H_2	-0.015	0.021	0.124	-0.320
	Cl1	-0.164	-0.469	0.091	0.731
	H1	0.009	-0.039	0.035	-0.016
	HCl	-0.155	-0.508	0.126	0.715
	IL anion	0.118	0.517	-0.291	-0.350
	IL cation	0.052	-0.030	0.040	-0.045
	IL	0.170	0.487	-0.251	-0.395
TPPT catalyst	H2	0.473	0.018	0.061	-0.109
	C1	0.030	0.015	-0.252	0.075
	C2	0.016	-0.024	0.437	-0.344
	H3	-0.052	0.012	0.028	-0.064
	C_2H_2	-0.007	0.022	0.274	-0.442
	Cl1	-0.099	0.037	-0.392	0.635
	H1	0.052	-0.019	0.096	-0.158
	HCl	-0.047	0.017	-0.296	0.477
	IL anion	0.047	-0.033	0.018	-0.029
	IL cation	0.013	-0.006	0.004	-0.006
	IL	0.061	-0.039	0.022	-0.035

Table S5c. Hirshfeld charge changes during acetylene hydrochlorination reaction

Catalyst	Group/ atom	ΔCharge (Co ads-free)	ΔCharge (IM-Co ads)	ΔCharge (TS-IM)	ΔCharge (Pr-TS)
TPPB catalyst	H2	-0.031	0.023	0.010	-0.042
	C1	0.007	-0.023	0.038	0.000
	C2	-0.025	0.048	0.129	-0.082
	H3	-0.011	-0.027	0.020	-0.029
	C_2H_2	-0.060	0.020	0.197	-0.153
	Cl1	-0.132	-0.348	0.082	0.439
	H1	-0.072	0.022	-0.027	-0.013
	HCl	-0.204	-0.325	0.055	0.426
	IL anion	0.190	0.331	-0.251	-0.236
	IL cation	0.074	-0.026	-0.001	-0.037
	IL	0.264	0.305	-0.252	-0.273
TPPC catalyst	H2	-0.031	0.023	0.002	-0.037
	C1	0.006	-0.019	0.014	0.019
	C2	-0.026	0.051	0.104	-0.060
	H3	-0.011	-0.027	0.025	-0.036
	C_2H_2	-0.063	0.029	0.145	-0.114
	Cl1	-0.160	-0.320	0.081	0.438
	H1	-0.071	0.042	-0.038	-0.025
	HCl	-0.231	-0.278	0.043	0.413
	IL anion	0.212	0.284	-0.187	-0.261
	IL cation	0.082	-0.034	-0.001	-0.038
	IL	0.294	0.250	-0.188	-0.299

BuTPPB catalyst	H2	-0.030	0.023	0.008	-0.042
	C1	0.006	-0.019	0.032	0.003
	C2	-0.027	0.049	0.123	-0.074
	H3	-0.011	-0.023	0.015	-0.028
	C_2H_2	-0.062	0.030	0.178	-0.141
	Cl1	-0.130	-0.315	0.032	0.453
	H1	-0.069	0.018	-0.025	-0.014
	HCl	-0.199	-0.297	0.007	0.439
	IL anion	0.203	0.342	-0.235	-0.264
	IL cation	0.058	-0.075	0.050	-0.034
	IL	0.261	0.267	-0.185	-0.298
TPPT catalyst	H2	-0.017	0.004	0.013	-0.036
	C1	0.004	0.033	0.048	-0.059
	C2	-0.029	0.024	0.213	-0.138
	H3	-0.012	0.007	0.031	-0.071
	C_2H_2	-0.054	0.068	0.305	-0.304
	Cl1	-0.066	0.041	-0.325	0.383
	H1	-0.028	0.000	0.002	-0.053
	HCl	-0.094	0.041	-0.323	0.330
	IL anion	0.302	-0.245	0.031	-0.047
	IL cation	-0.154	0.136	-0.013	0.021
	IL	0.148	-0.109	0.018	-0.026

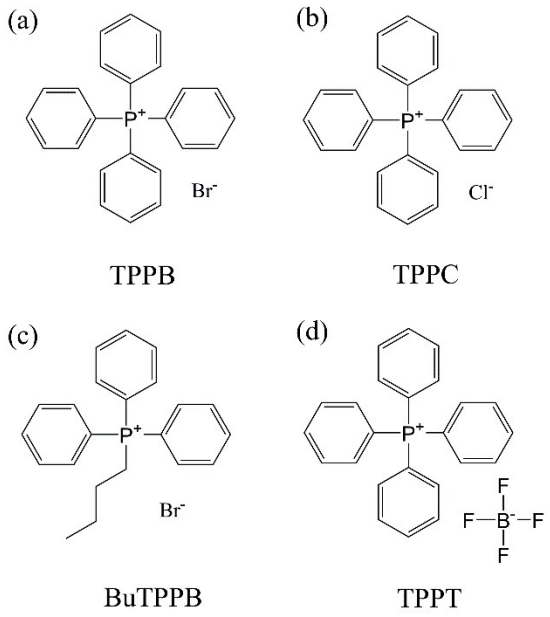

Figure S1. Structural formulas of (a) TPPB, (b) TPPC, (c) BuTPPB and (d) TPPT ILs.

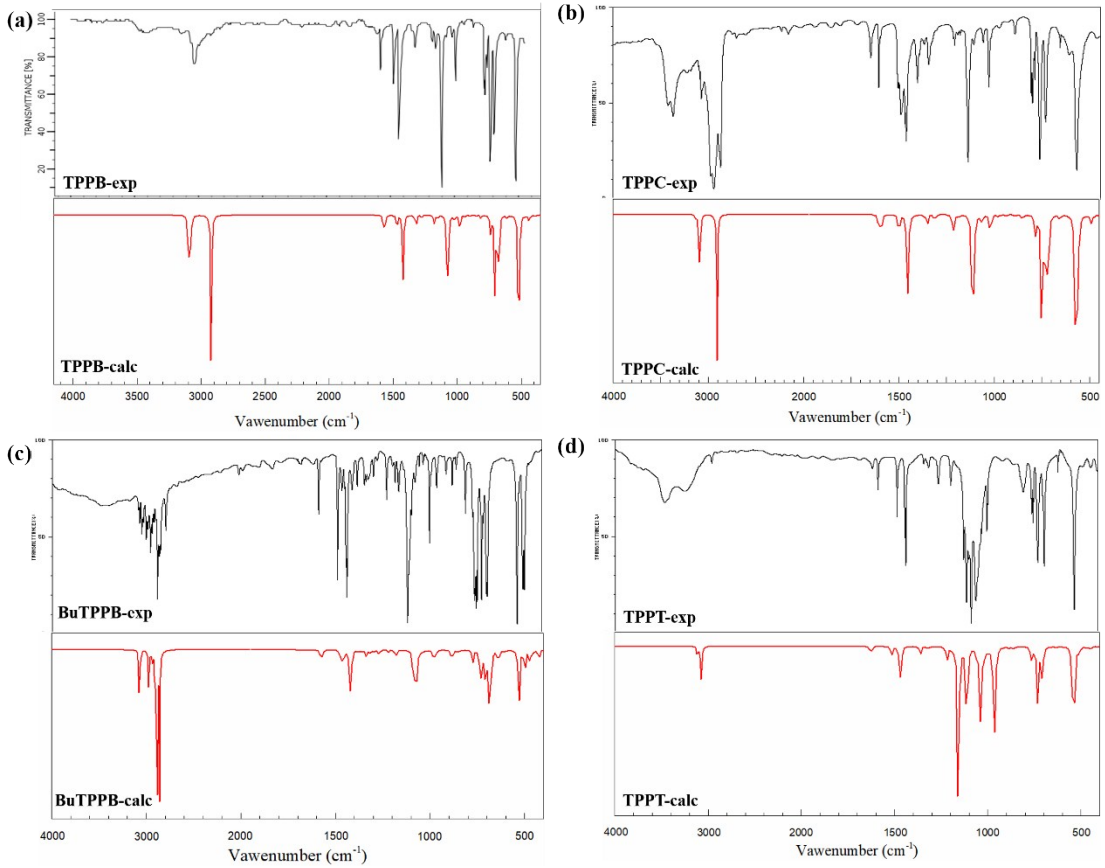

Figure S2. Calculated IR spectra and standard IR spectra for TPPB (a), TPPC (b), BuTPPB (c) and TPPT (d).

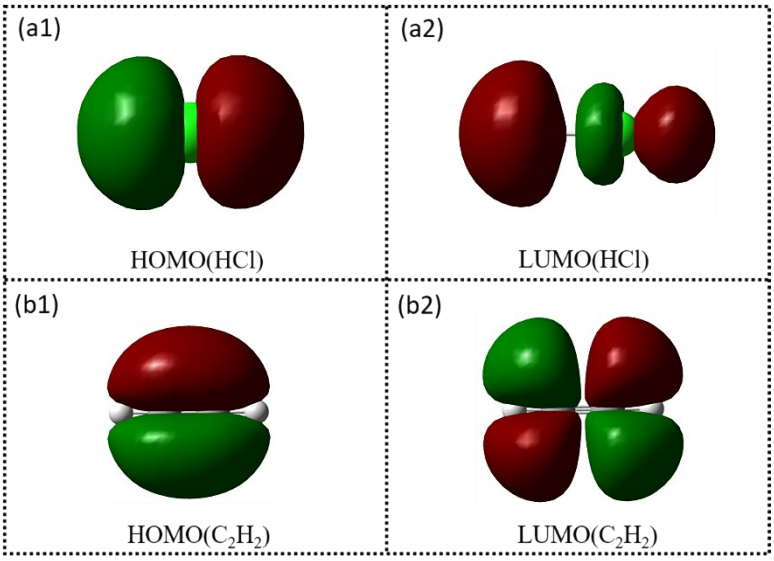

Figure S3. HOMO orbital of (a1) HCl, (b1) C_2H_2 and LUMO orbital of (a2) HCl, (b2) C_2H_2 (isosurface=0.05).

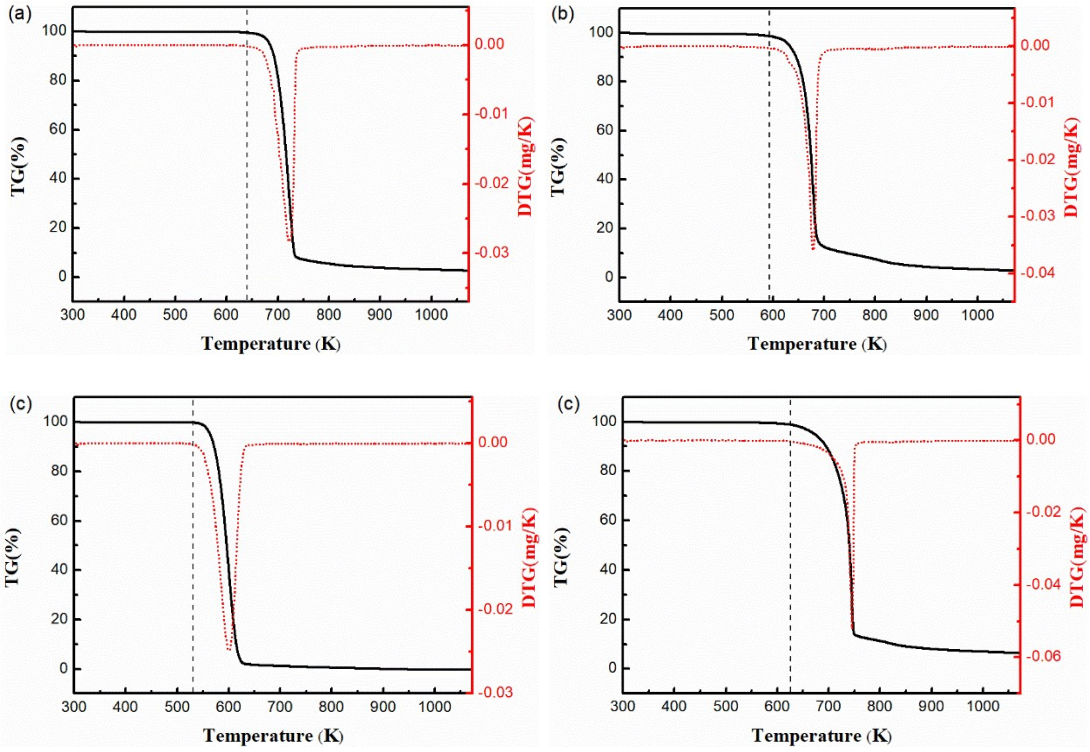

Figure S4. TGA curves of the TPPB (a), TPPC (b), BuTPPB (c) and TPPT (d).

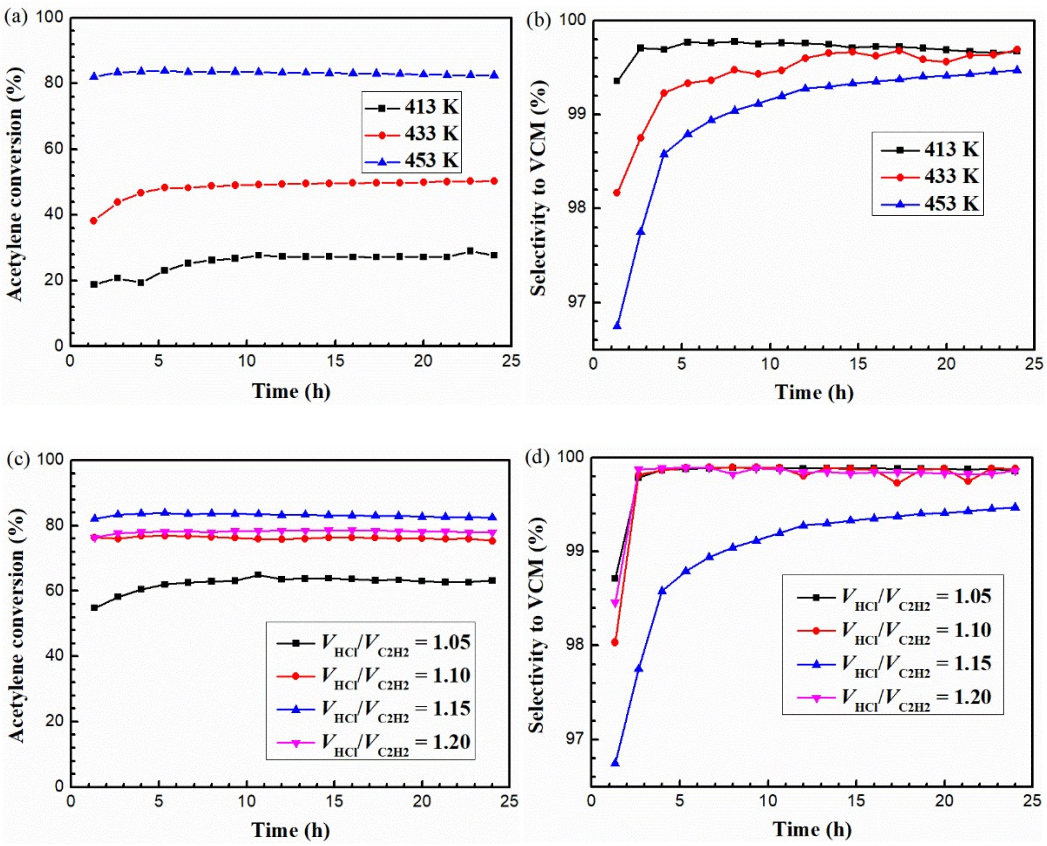

Figure. S5 Conversion of acetylene (a) and selectivity to VCM (b) over 15%TPPB/SAC under different reaction temperature from 413 K to 453 K, with of *GHSV* (C_2H_2) = 50 h^{-1} and V_{HCl}/V_{C2H2} =1.15. Conversion of acetylene (c) and selectivity to VCM (d) over 15%TPPB/SAC under different V_{HCl}/V_{C2H2} from 1.05 to 1.20, with of Temperature = 453 K and *GHSV* (C_2H_2) = 50 h^{-1}.

The effect of the pressure has not been considered and the effect of reaction temperature and HCl/C_2H_2 feeding volume ratio (V_{HCl}/V_{C2H2}) was investigated, as shown in Figure S5. Because the reaction temperature is 413 K in the industrial operations[18, 19], the reaction temperatures of 413 K, 433 K and 453 K were chosen here. The acetylene conversion over 15%TPPB/SAC catalyst is increased with the reaction temperature, and the VCM selectivity

is above 99% after several hour reaction. Considering the energy consumption in the reaction as well as the general temperature used in the previous work, which was 443 K ~ 453 K[20-22], the optimal temperature was set at 453 K.

The effect of V_{HCl}/V_{C2H2} were studied by vary V_{HCl}/V_{C2H2} from 1.05 to 1.20 (shown in Figure R1c and d). For acetylene hydrochlorination reaction, excessive content of HCl compared with C_2H_2 can inhibit the formation of carbon deposition by the polymerization of C_2H_2 and VCM[23]. When the ratio of V_{HCl}/V_{C2H2} increased from 1.05 to 1.15, the acetylene conversion is gradually increased from 65% to 84%, whereas it is decreased to 78% when the V_{HCl}/V_{C2H2} equals 1.20. Although the VCM selectivity is the lowest as V_{HCl}/V_{C2H2} = 1.15, it is still over 99% after several hour reaction. Thus, the optimal V_{HCl}/V_{C2H2} was set at 1.15.

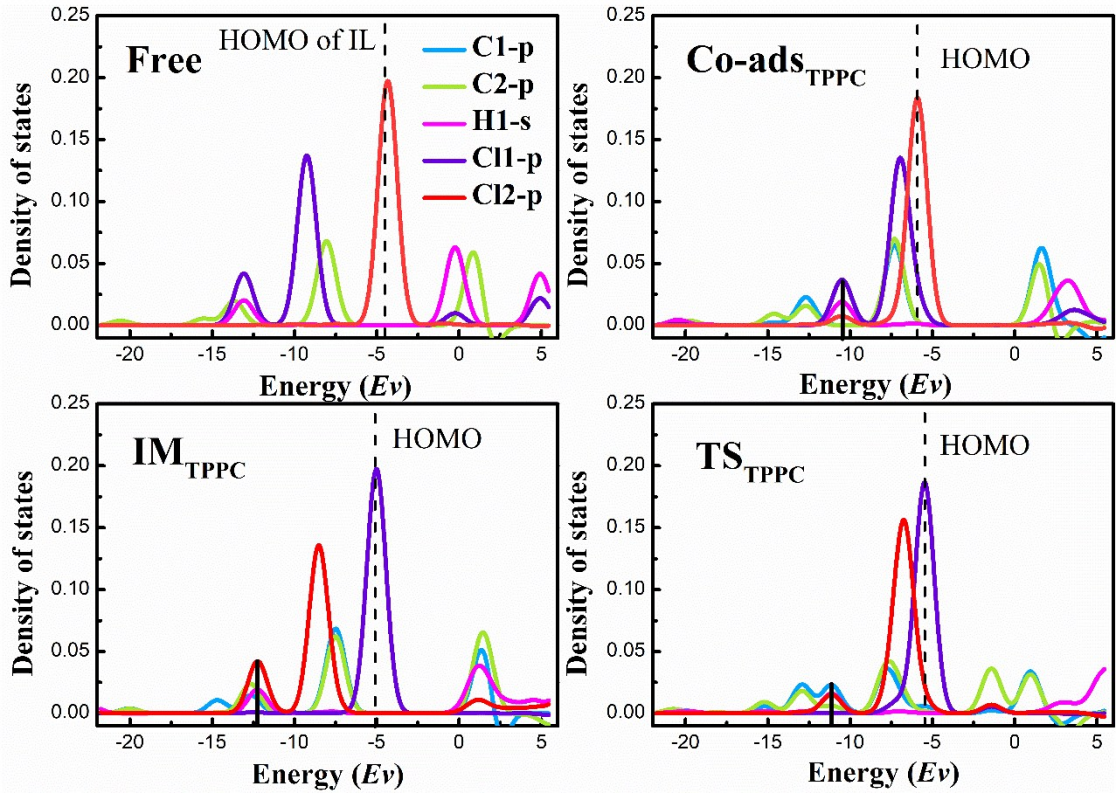

Figure S6. PDOS of catalytic reaction process on TPPC

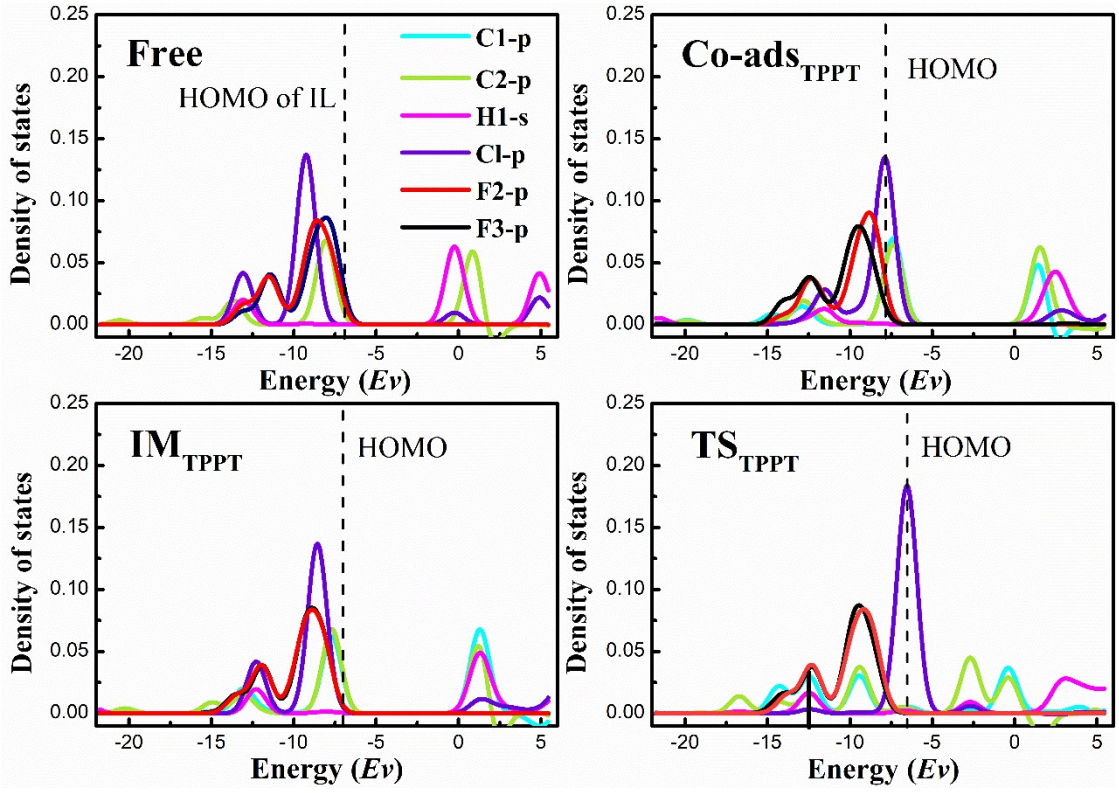

Figure S7. PDOS of catalytic reaction process on TPPT

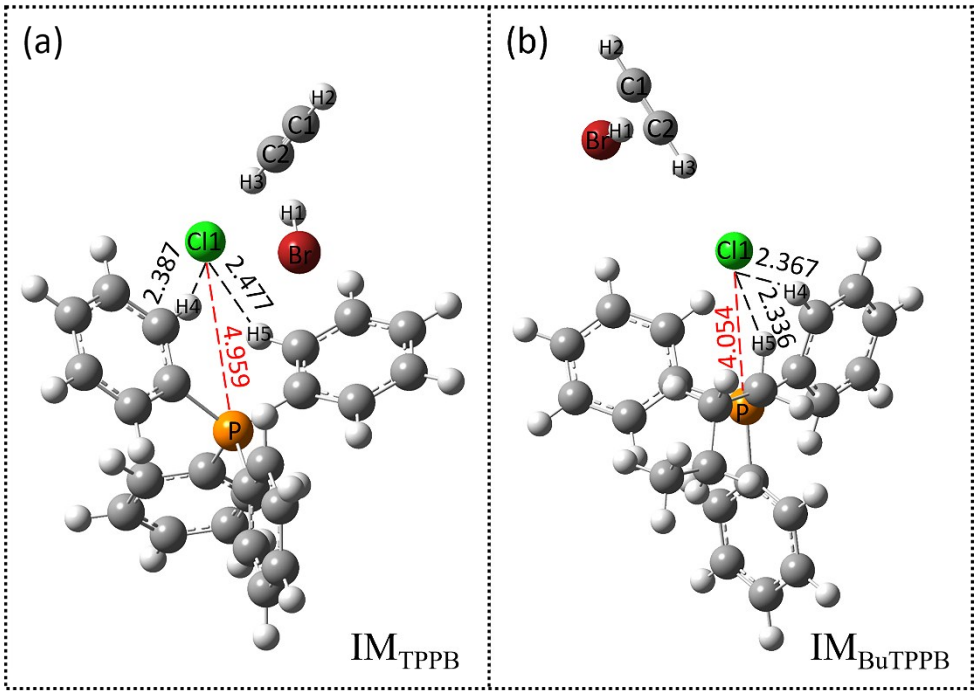

Figure S8. Hydrogen bonds in IM_{TPPB} and IM_{TPPT} configurations

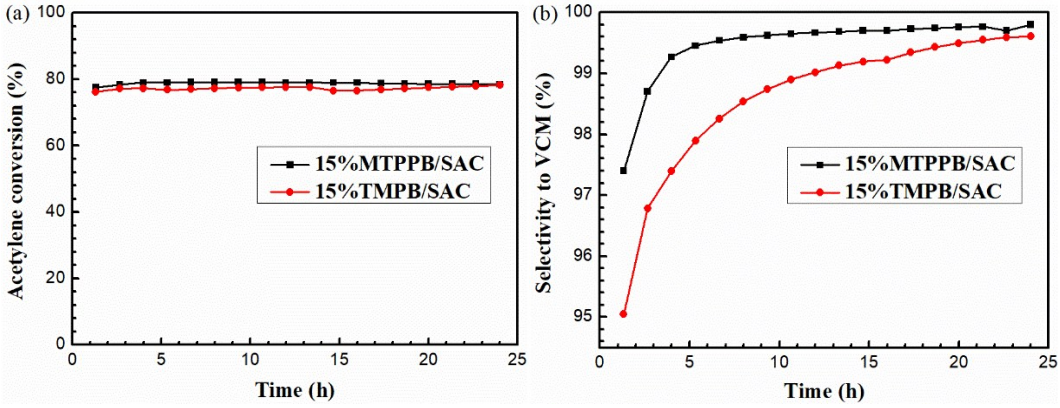

Figure S9. C_2H_2 conversion (a) and VCM selectivity (b) over 15%MTPPB/SAC and 15%TMPB/SAC catalysts under reaction conditions of T = 453 K, *GHSV* (C_2H_2) = 50 h^{-1} and V_{HCl}/V_{C2H2} = 1.15.

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