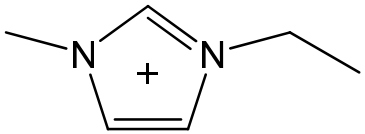
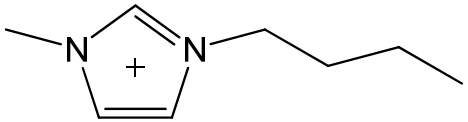
1. Structures and abbreviations of cations and anions used in this study

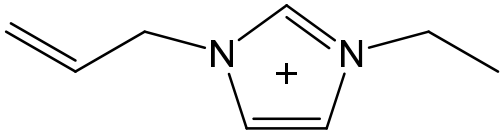
Cations



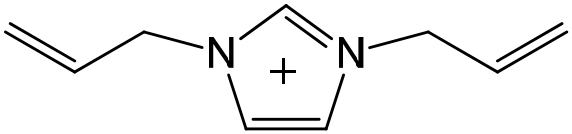
[EMIm]$^+$: 1-ethyl-3-methylimidazolium



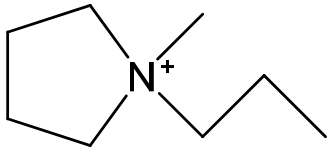
[BMIm]$^+$: 1-butyl-3-methylimidazolium



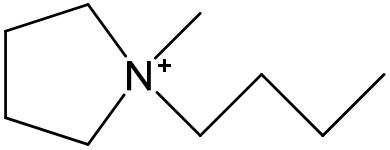
[AEIm]$^+$: 1-allyl-3-ethylimidazolium



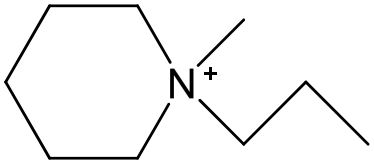
[AAIm]$^+$: 1,3-Diallylimidazolium



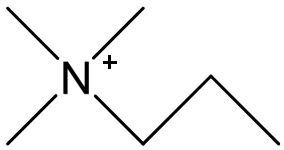
[P_{13}]$^+$: *N*-methyl-*N*-propylpyrrolidinium



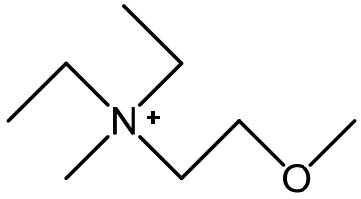
[P_{14}]$^+$: *N*-butyl-*N*-methylpyrrodinium



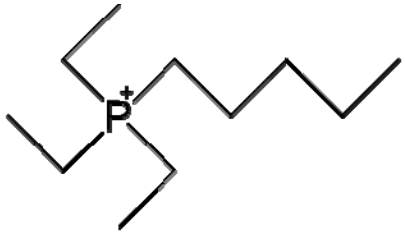
[Pp_{13}]$^+$: *N*-methyl-*N*-propylpiperidinium



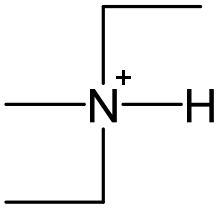
[$N_{1,1,1,3}$]$^+$:*N,N,N*-trimethyl-*N*- propylammonium



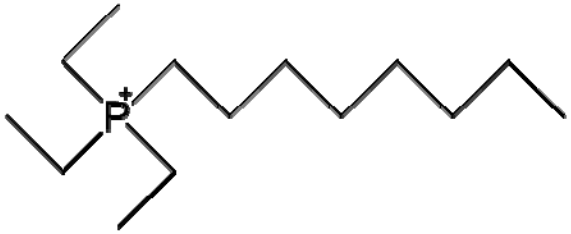
[DEME]$^+$: *N,N*-Deithyl-*N*-methyl-N-(2-methoxy ethyl)ammonium



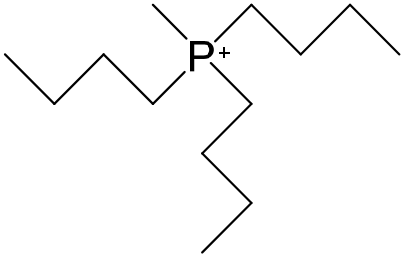
[$P_{2,2,2,5}$]$^+$: pentyltriethylphosphonium



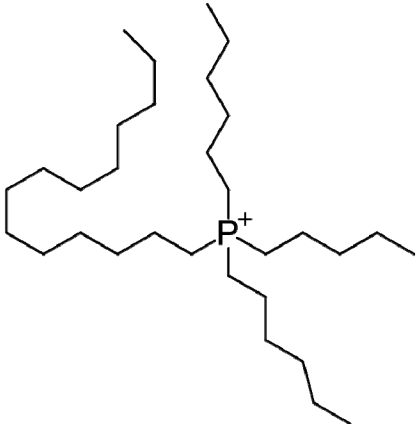
[DEMAH]: *N*-methyl-*N,N*-ethylammonium



$[P_{2,2,2,8}]^+$: Octyltriethylphosphonium

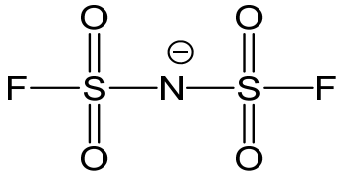


$[P_{4,4,4,1}]^+$: methyltributylphosphonium

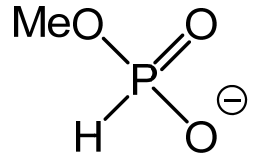


$[P_{6,6,6,14}]^+$: tetradecyltrihexylphosphonium

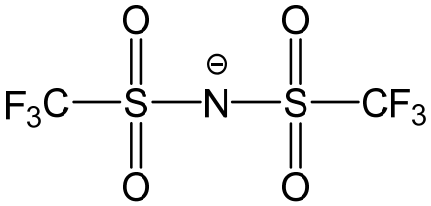
Anions



$[Nf_2]^-$: bis(fluorosulfonyl)amide



$[(MeO)(H)PO_2]^-$: methylphosphonate

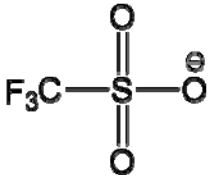


$[NTf_2]^-$: bis(trifluoromethanesulfonyl)amide

Cl^-

$[PF_6]^-$: hexafluorophosphate

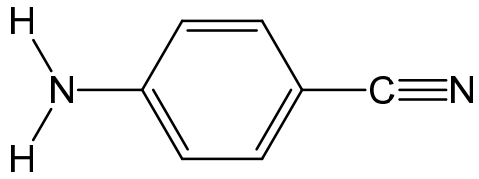
$[BF_4]^-$:tetrafluoroborate



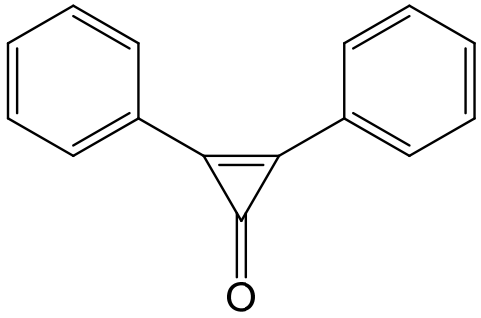
$[TfO]^-$: trifluoromethanesulfonate

2. Molecular structures used as probes in this study.

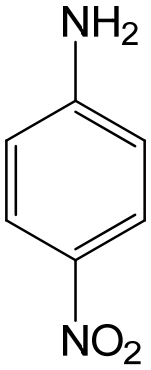
p-Aminobenzonitrile (ABN)



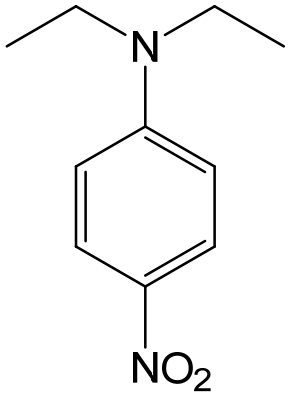
Diphenylcyclopropenone (DPCP)



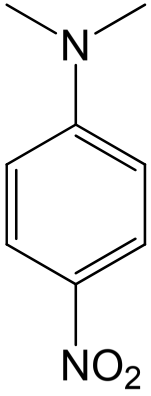
p-Nitroanilne (pNA)



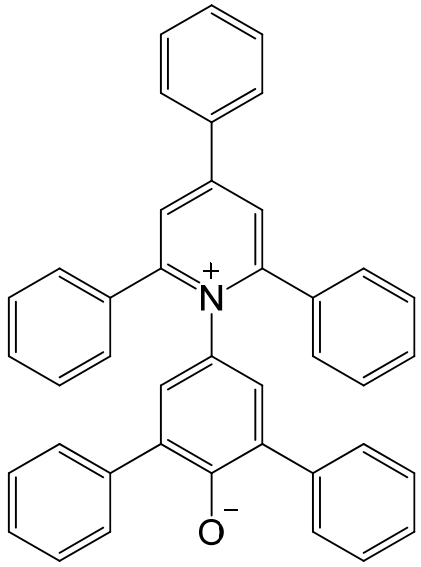
*N,N-D*iethyl-*p*-nitroan ilne (DEPNA)



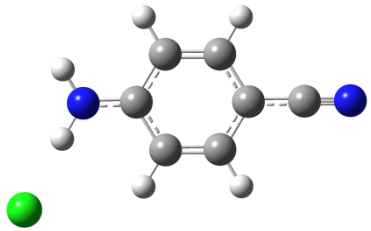
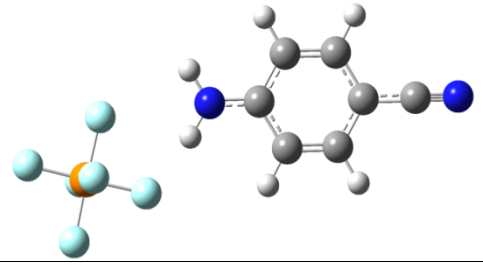
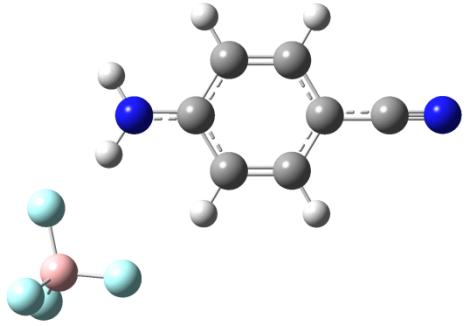
*N,N-D*imethyl-*p*-nitroa nilne (DMPNA)

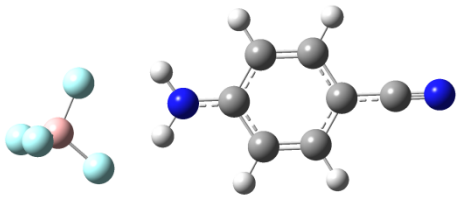
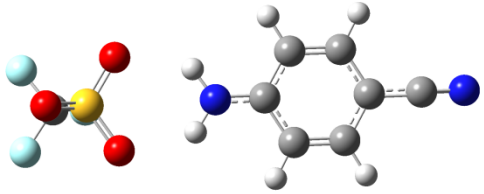
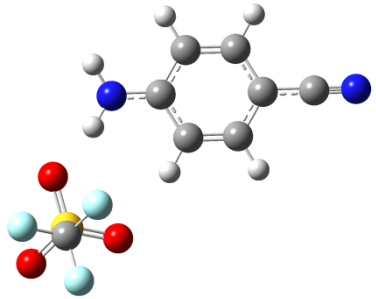
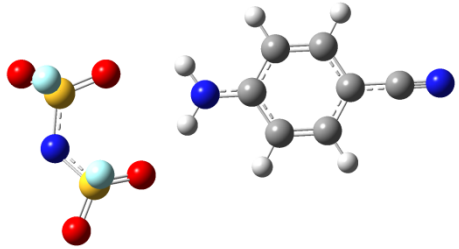
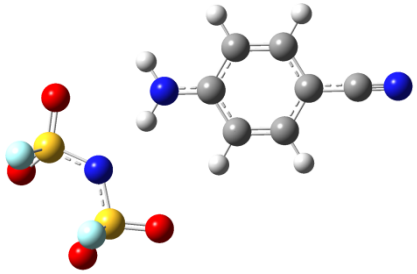


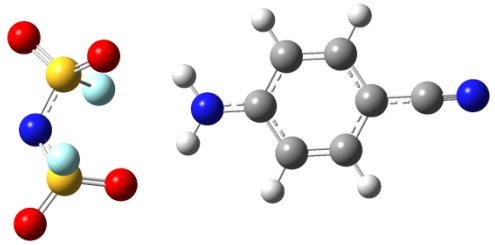
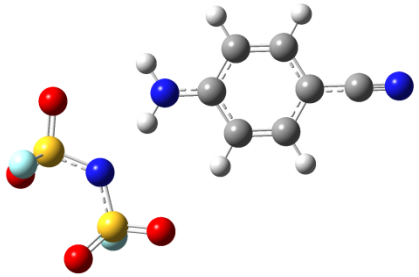
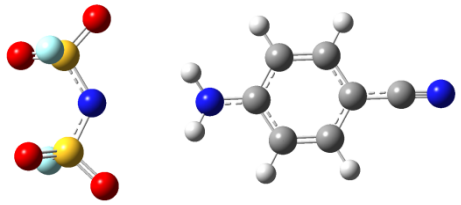
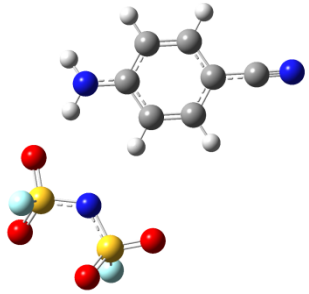
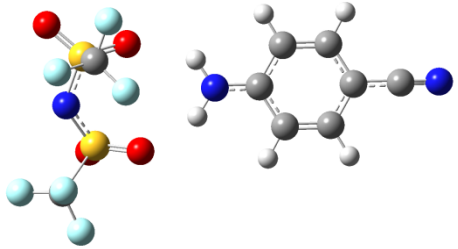
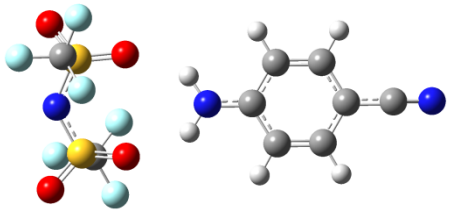
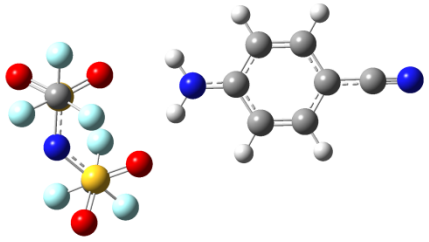
Reichardt dye



3. Table of Stabilization energy of the cluster and the relative shift of the vibrational frequencies of CN and NH_2 stretching modes calculated by DFT (B3PW91 functional and 6-311G++(d,p) basis set) using Gaussian 09.

Anion	Symmetric	Asymmetirc
Cl^-		(a)  ΔE = -25.21 kcal mol^{-1} $\Delta\nu_{NH2}$ = -668.86 cm^{-1} $\Delta\nu_{CN}$ = -34.81 cm^{-1}
PF_6^-		(b)  ΔE = -16.07 kcal mol^{-1} $\Delta\nu_{NH2}$ = -92.06 cm^{-1} $\Delta\nu_{CN}$ = -24.92 cm^{-1}
BF_4^-		(c)  ΔE = -18.61 kcal/mol $\Delta\nu_{NH2}$ = -190.15 cm^{-1} $\Delta\nu_{CN}$ = -26.35 cm^{-1}

		(d)  ΔE = -19.38 kcal mol^{-1} $\Delta\nu_{NH2}$ = -99.08 cm^{-1} $\Delta\nu_{CN}$ = -28.21 cm^{-1}
TfO^-	(e)  ΔE = -19.45 kcal mol^{-1} $\Delta\nu_{NH2}$ = -85.27 cm^{-1} $\Delta\nu_{CN}$ = -28.24 cm^{-1}	(f)  ΔE = -18.92 kcal mol^{-1} $\Delta\nu_{NH2}$ = -279.93 cm^{-1} $\Delta\nu_{CN}$ = -26.83 cm^{-1}
Nf_2^-		(g)  ΔE = -16.74 kcal mol^{-1} $\Delta\nu_{NH2}$ = -76.56 cm^{-1} $\Delta\nu_{CN}$ = -25.24 cm^{-1}
		(h)  ΔE = -16.76 kcal mol^{-1} $\Delta\nu_{NH2}$ = -165.24 cm^{-1} $\Delta\nu_{CN}$ = -24.78 cm^{-1}

	(i)		ΔE = -16.60 kcal mol^{-1} $\Delta\nu_{NH2}$ = -49.01 cm^{-1} $\Delta\nu_{CN}$ = -25.28 cm^{-1}	(j)		ΔE = -16.71 kcal mol^{-1} $\Delta\nu_{NH2}$ = -167.93 cm^{-1} $\Delta\nu_{CN}$ = -24.65 cm^{-1}
	(k)		ΔE = -12.38 kcal mol^{-1} $\Delta\nu_{NH2}$ = -70.86 cm^{-1} $\Delta\nu_{CN}$ = -19.81 cm^{-1}	(l)		ΔE = -14.64 kcal mol^{-1} $\Delta\nu_{NH2}$ = -123.76 cm^{-1} $\Delta\nu_{CN}$ = -20.39 cm^{-1}
NTf_2^-	(m)		ΔE = -16.92 kcal mol^{-1} $\Delta\nu_{NH2}$ = -58.89 cm^{-1} $\Delta\nu_{CN}$ = -25.64 cm^{-1}			
	(n)		ΔE = -16.89 kcal mol^{-1} $\Delta\nu_{NH2}$ = -40.84 cm^{-1} $\Delta\nu_{CN}$ = -24.54 cm^{-1}	(o)		ΔE = -16.89 kcal mol^{-1} $\Delta\nu_{NH2}$ = -89.77 cm^{-1} $\Delta\nu_{CN}$ = -25.37 cm^{-1}

4. Correlation of the CN stretching frequency using the traditional parameters.

$$\nu_{CN} = 2228.4 - 8.7818\pi^* + 2.3834\alpha - 10.692\beta$$