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

Supporting Information

Screening of metal complexes and organic solvents using COSMOSAC-LANL model to enhance the energy density in non-aqueous redox flow cell: an insight into the solubility

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1 Error estimation from coefficient of determination (R^2)

For a linear function, $y = (y_1 \cdots\cdots y_n)$ of input $y = (y_1 \cdots\cdots y_n)$, the a and b of smallest residual is

$$(a, b) = arg\min \sum_i (y_i - ax_i - b)^2 \,, \tag{1}$$

which gives you $a = arg\min var(y - ax)$, $b = \bar{y} - a\bar{x}$ and $R^2 = \frac{var(ax)}{Var(y)} = corr(x, y)$, where for any two vectors $u, v, \bar{u}$ is the empirical mean. $var(u)$ and $corr(u, v)$ the correlation.

Now, $var(y - ax)$ is equal to (1-R^2)*$var(y)$. By normalizing errors by $var(y)$, one will obtain

$$Error = \frac{var(y - ax)}{var(y)} = 1 - R^2 \,. \tag{2}$$

Now 'error' is the root mean error divided by the standard deviation of the output and which is $\sqrt{Error}$.

Table S 1: The details of COSMO setting for the metal complexes

XC potential in SCF: **GGA: BP**	Solvation method: **COSMO**
XC energy after SCF: **Default**	Solvent: **CRS**
Relativity (ZORA): **Scalar**	Default radii: **Klamt**
XC: **Becke Perdew**	Surface: **Delley**
Basis set: **TZP**	Ndiv: **4**
Frozen core: **Small**	Charge determination method: **CONJ**
Integration: **Becke Good**	Convergence: **1.00E-06**
Density used in exchange potential: **Exact**	Max. iterations: **300**
Total charge: **0.0**	Correct for outlying charge: **Yes**
Spin polarization: **2.0 - 3.0**	Calculate coulomb interaction: **EXACT**
Coordinates used for optimization: **Delocalized**	Disc scaling: **0.01**
Optimization method: **new**	Disc Legendre order: **4**
Number of geometry iterations: **100**	Disc tolerance: **0.1**
Maximum no of SCF cycles: **50**	Handle charges: **VAR**
Convergence method: **DIIS**	Charges in which SCF cycles: **ALL**
Mixing: **0.2**	–

Table S 2: The details of COSMO setting for the organic solvents

XC potential in SCF: **GGA: BP**	Solvation method: **COSMO**
XC energy after SCF: **Default**	Solvent: **CRS**
Relativity (ZORA): **Scalar**	Default radii: **Klamt**
XC: **Becke Perdew**	Surface: **Delley**
Basis set: **TZP**	Ndiv: **4**
Frozen core: **Small**	Charge determination method: **CONJ**
Integration: **Becke Good**	Convergence: **1.00E-06**
Density used in exchange potential: **Exact**	Max. iterations: **300**
Total charge: **0.0**	Correct for outlying charge: **Yes**
Spin polarization: **0.0**	Calculate coulomb interaction: **EXACT**
Coordinates used for optimization: **Delocalized**	Disc scaling: **0.01**
Optimization method: **new**	Disc Legendre order: **4**
Number of geometry iterations: **100**	Disc tolerance: **0.1**
Maximum no of SCF cycles: **50**	Handle charges: **VAR**
Convergence method: **DIIS**	Charges in which SCF cycles: **ALL**
Mixing: **0.2**	–

Table S 3: The details of frequency calculations.

Basis set	TZP
Frozen Core	Small
Task	GO & Frequency calculation
XC	Becke Perdew
Frequency	Analytical
Numerical quality	Excellent

Table S 4: Margules parameters of metal complexes in acetonitrile organic solvent at 297 K , COSMO Volume and COSMO Surface

Organic solvents	γ_{12}	A_{12}	γ_{21}	A_{21}	COSMO Volume (Å^3)	COSMO Surface (Å^2)
I	1.14	0.08	0.76	-0.16	387.35	357.69
II	1.058	0.03	0.75	-0.17	383.47	357.32
III	1.11	0.06	0.77	-0.16	379.83	353.29
IV	1.08	0.05	0.74	-0.18	393.18	351.10
V	0.96	-0.02	0.73	-0.19	389.56	362.22
VI	0.54	-0.36	0.43	-0.49	769.95	637.70
VII	1.82	0.35	0.47	-0.44	830.02	657.92
VIII	0.12	-1.26	0.32	-0.67	953.15	798.82
IX	0.06	-1.63	0.33	-0.65	866.90	728.61
X	0.02	-2.30	0.27	-0.78	1089.89	921.52
XI	0.26	-0.80	0.56	-0.35	460.46	411.09
XII	3.58	0.753	1.11	0.062	470.97	421.89
XIII	0.12	-1.27	0.45	-0.47	520.23	460.10

Table S 5: Margules parameters of $V(acac)_3$ in 14 different organic solvents at 297 K.

Numbers	Organic solvents	γ_{12}	A_{12}	γ_{21}	A_{21}
1	Cyclohexane	73.63	2.54	2.61	0.57
2	Diisopropyl Ether	1.47	0.23	1.13	0.07
3	1-Butanol	2.07	0.43	1.87	0.37
4	1-Hexanol	2.76	0.60	2.28	0.49
5	1-Hexyne	0.50	-0.41	0.73	-0.19
6	1-Heptyne	0.74	-0.18	0.87	-0.08
7	1-Hexene	8.29	1.25	1.74	0.33
8	Benzene	1.38	0.19	0.90	-0.06
9	1,3do	0.44	-0.48	0.66	-0.25
10	ACN	1.14	0.08	0.76	-0.16
11	DMPU	0.53	-0.38	0.71	-0.20
12	GBL	0.70	-0.21	0.82	-0.11
13	MA	0.54	-0.36	0.71	-0.21
14	PC	1.72	0.32	1.08	0.05

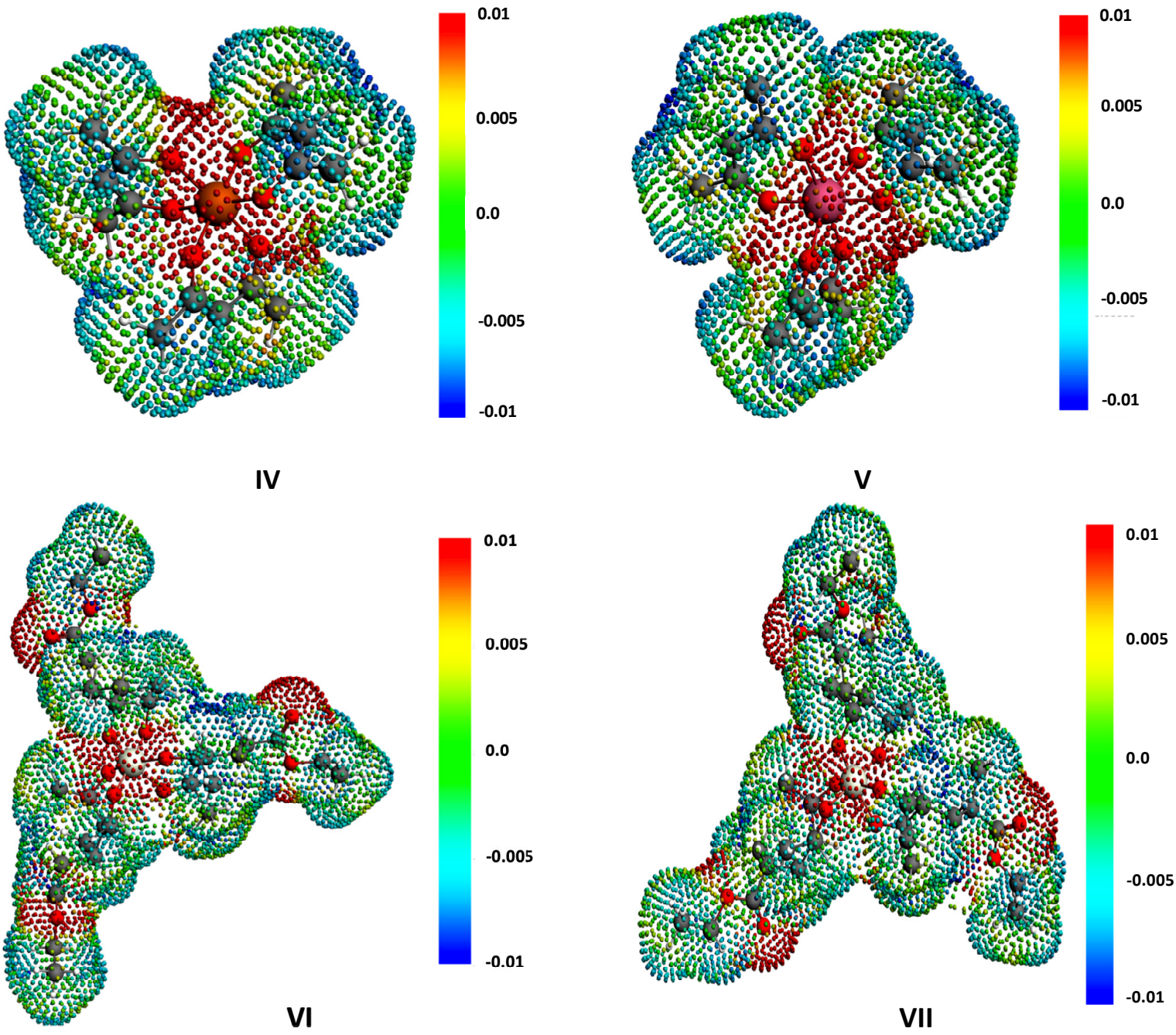


Figure. S 1: COSMO Surface points of metal complexes.

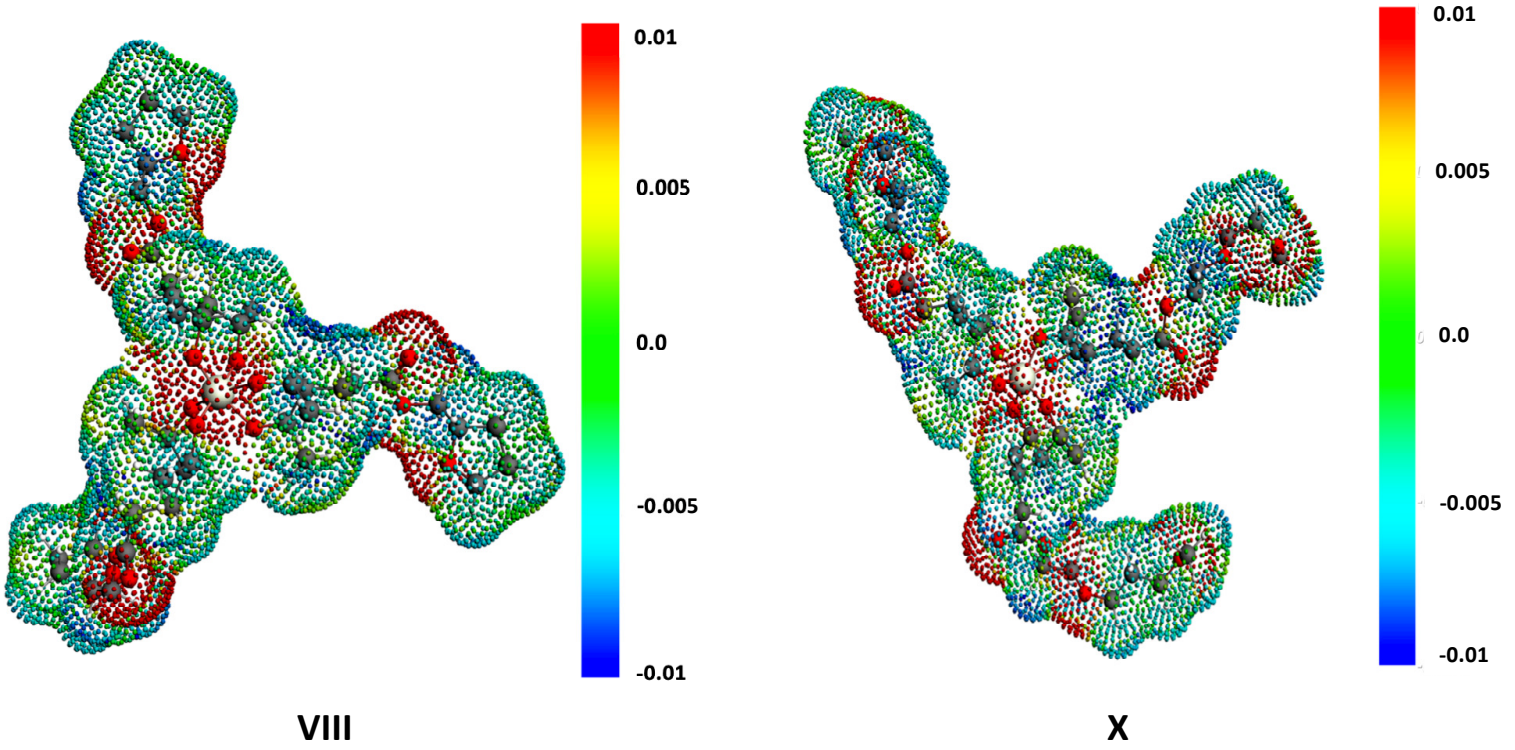


Figure. S 2: COSMO Surface points of metal complexes.

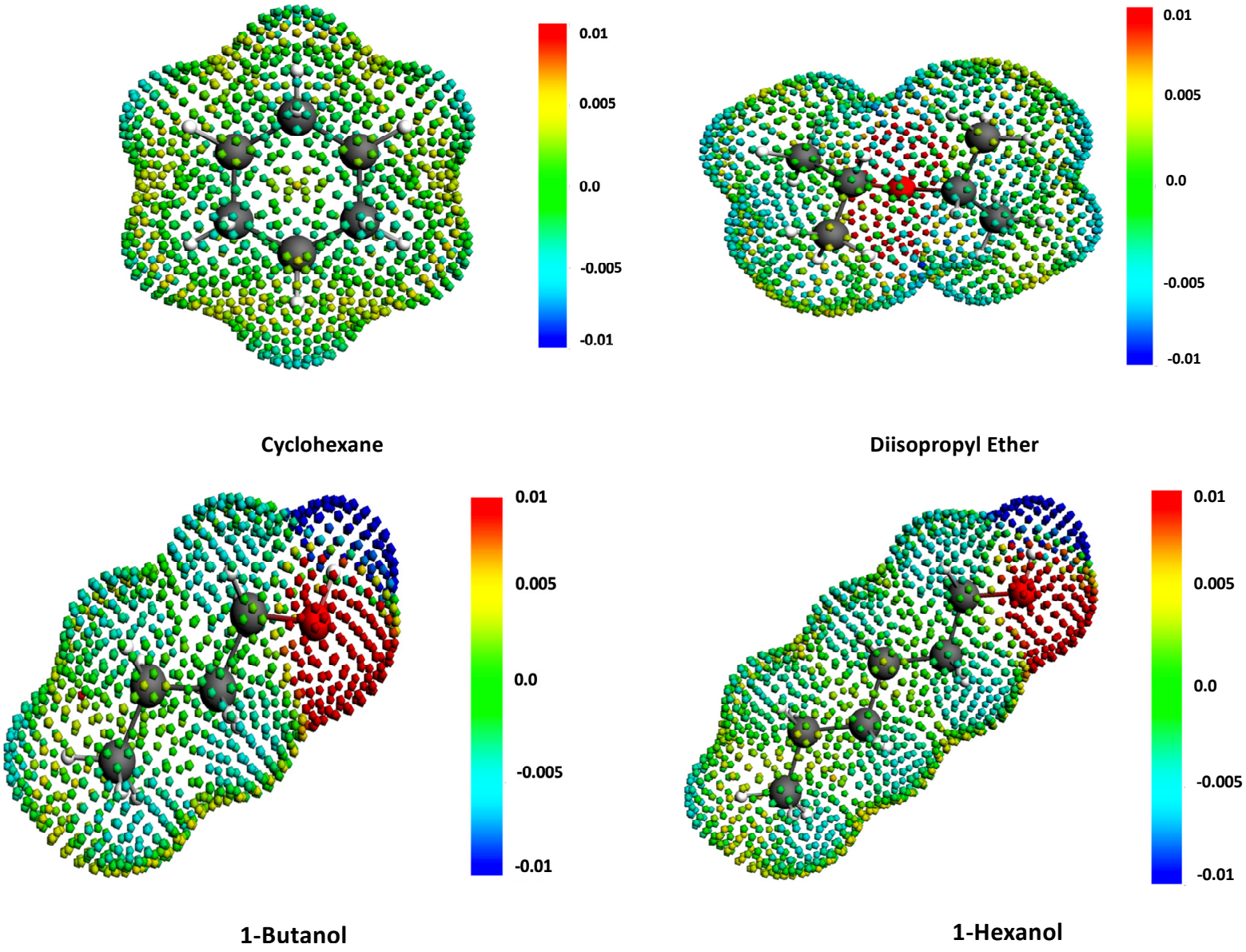


Figure. S 3: COSMO surface points of organic solvents.

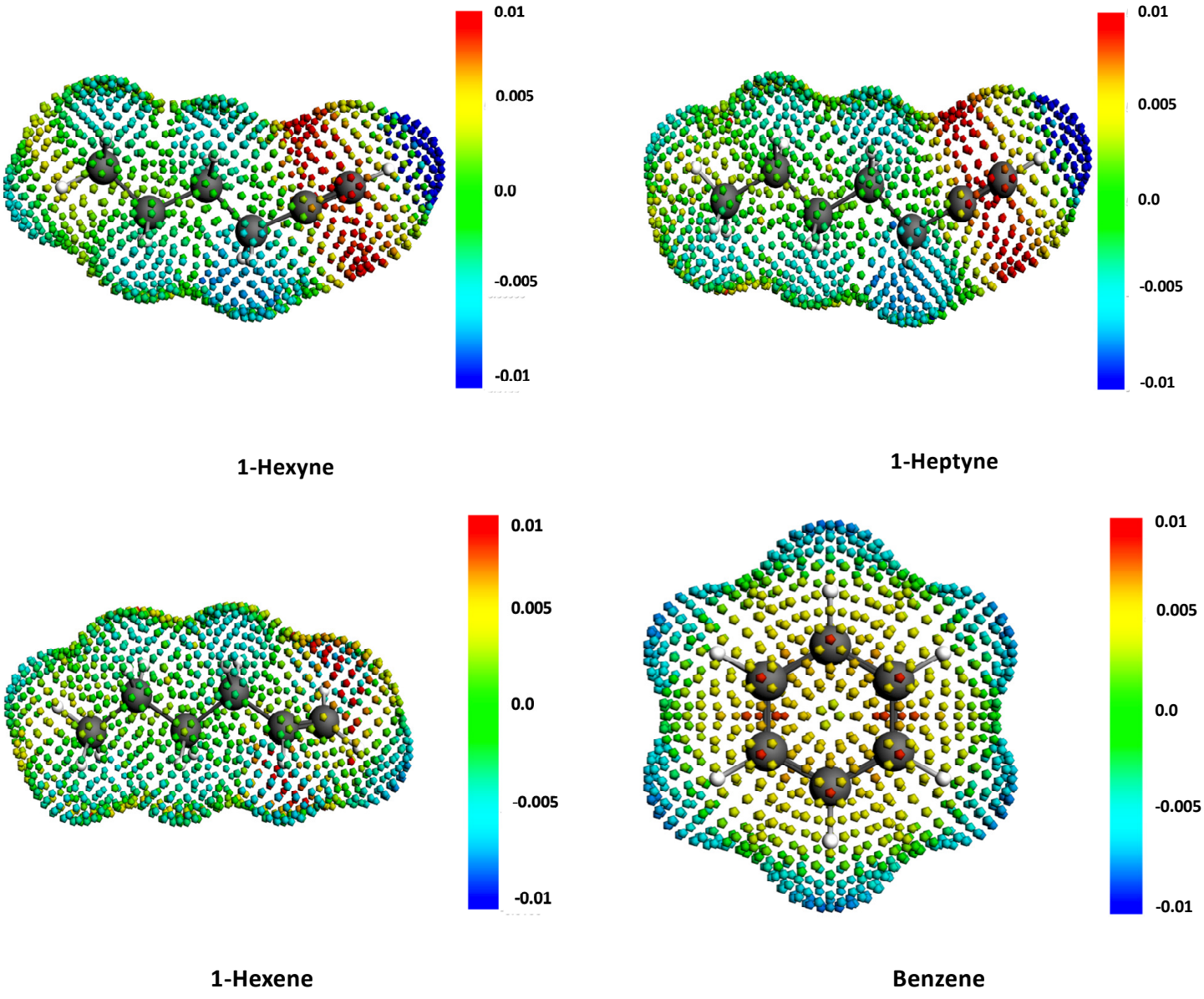


Figure. S 4: COSMO surface points of organic solvents.

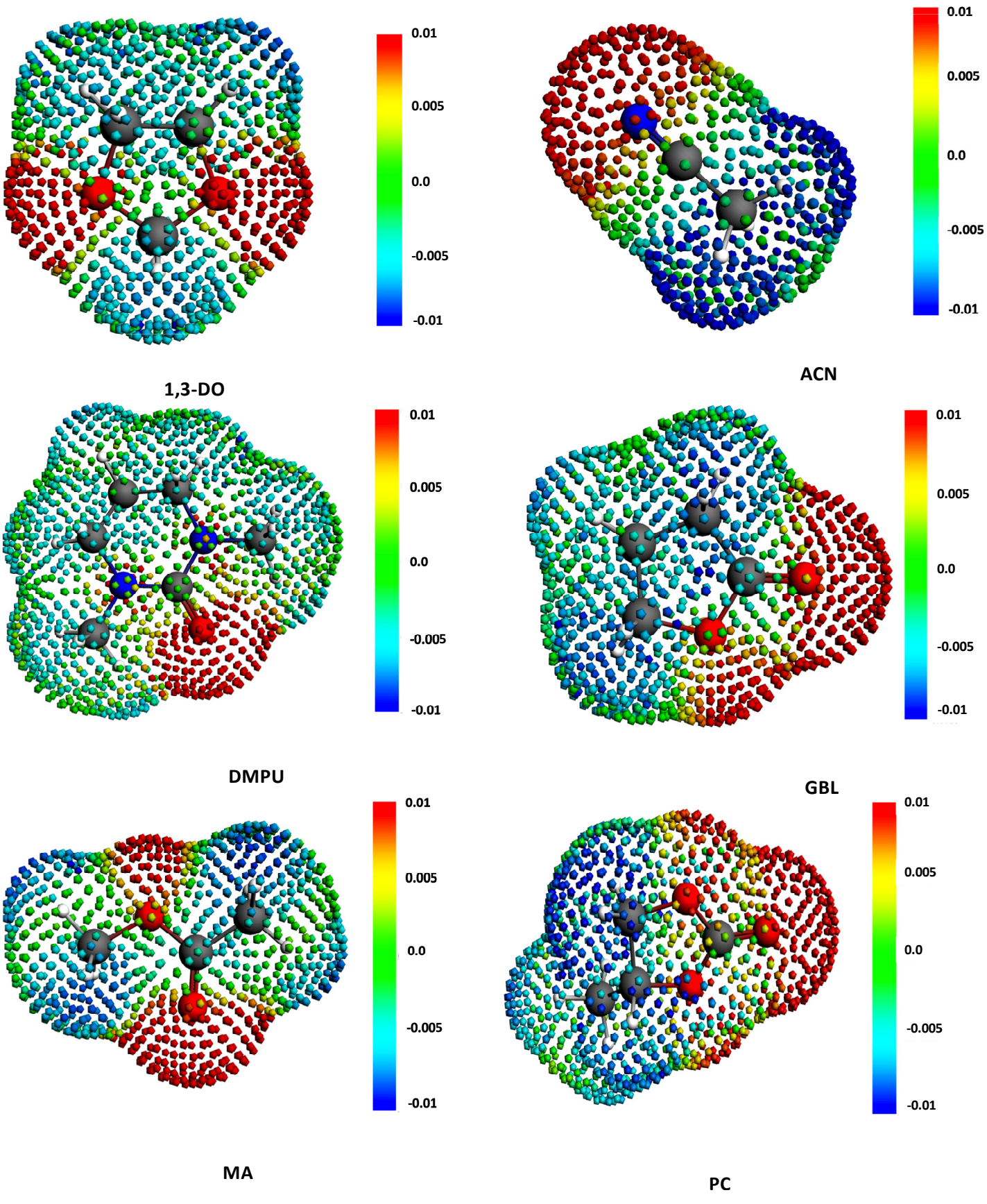


Figure. S 5: COSMO surface points of organic solvents.

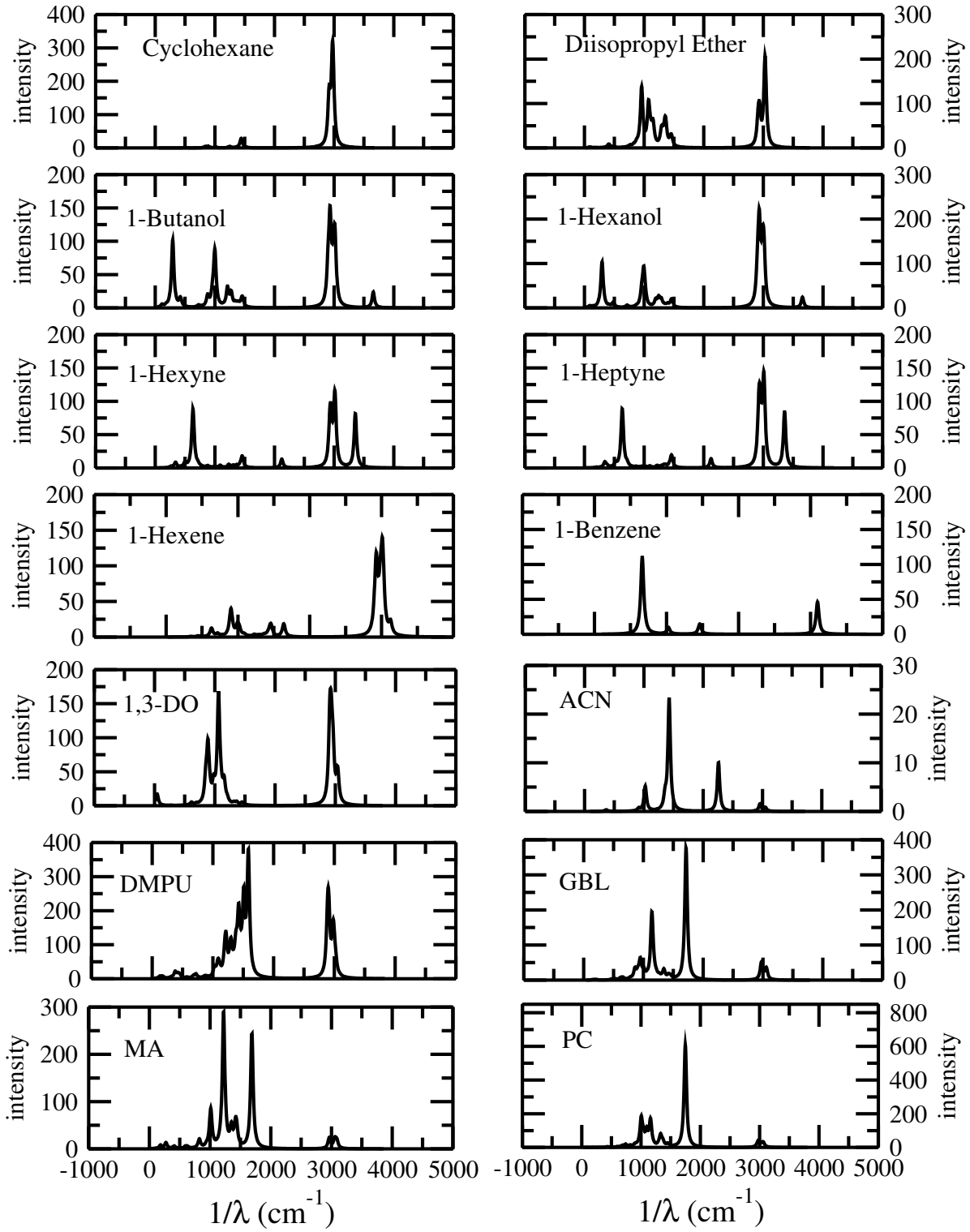


Figure. S 6: Analytical frequency of 14 different organic solvents at ambient condition.

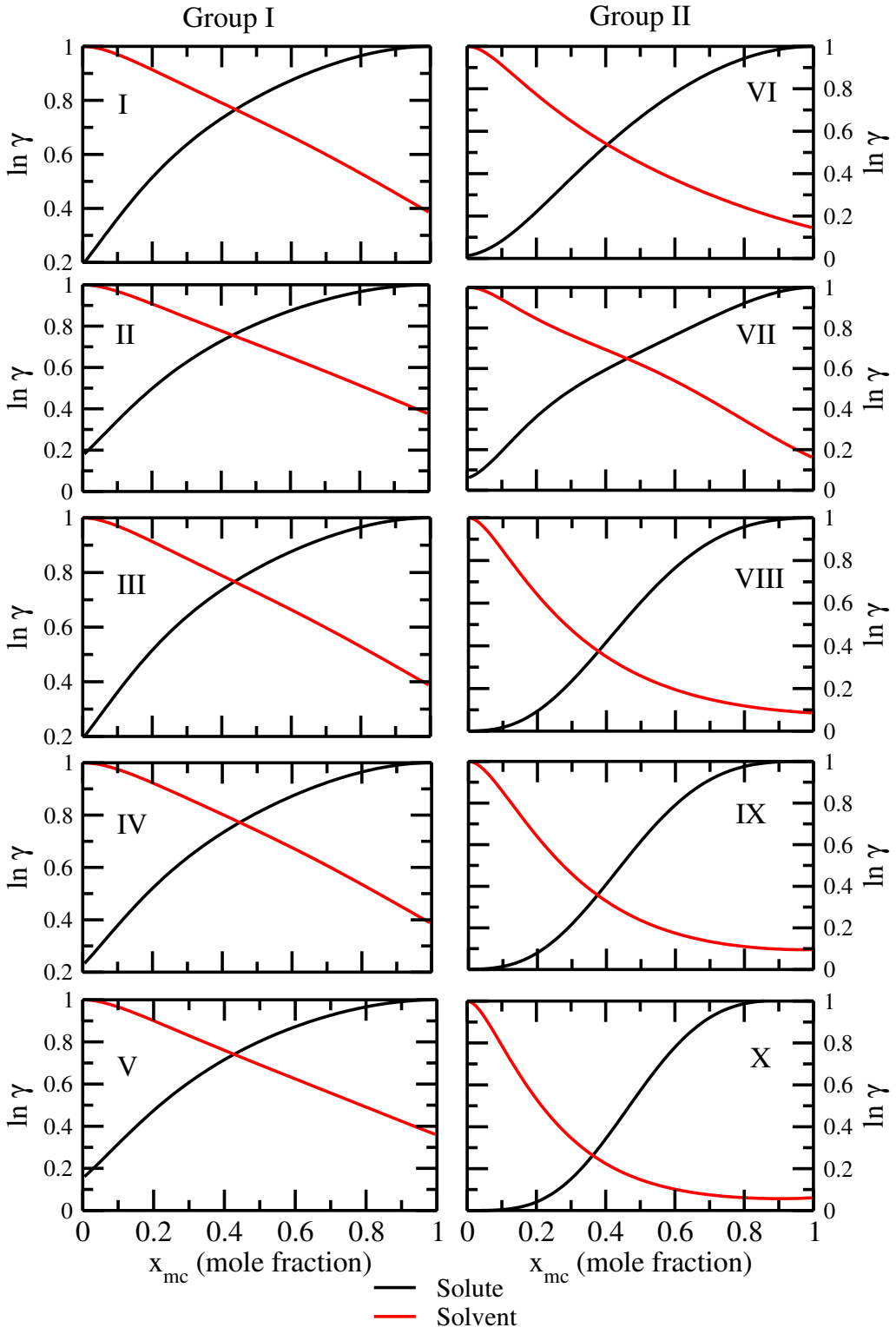


Figure. S 7: Gibbs-Duhem relationship of Group I and II type of metal complexes in acetonitrile solvent. The black curve is for the solute and the red curve is for the solvent.

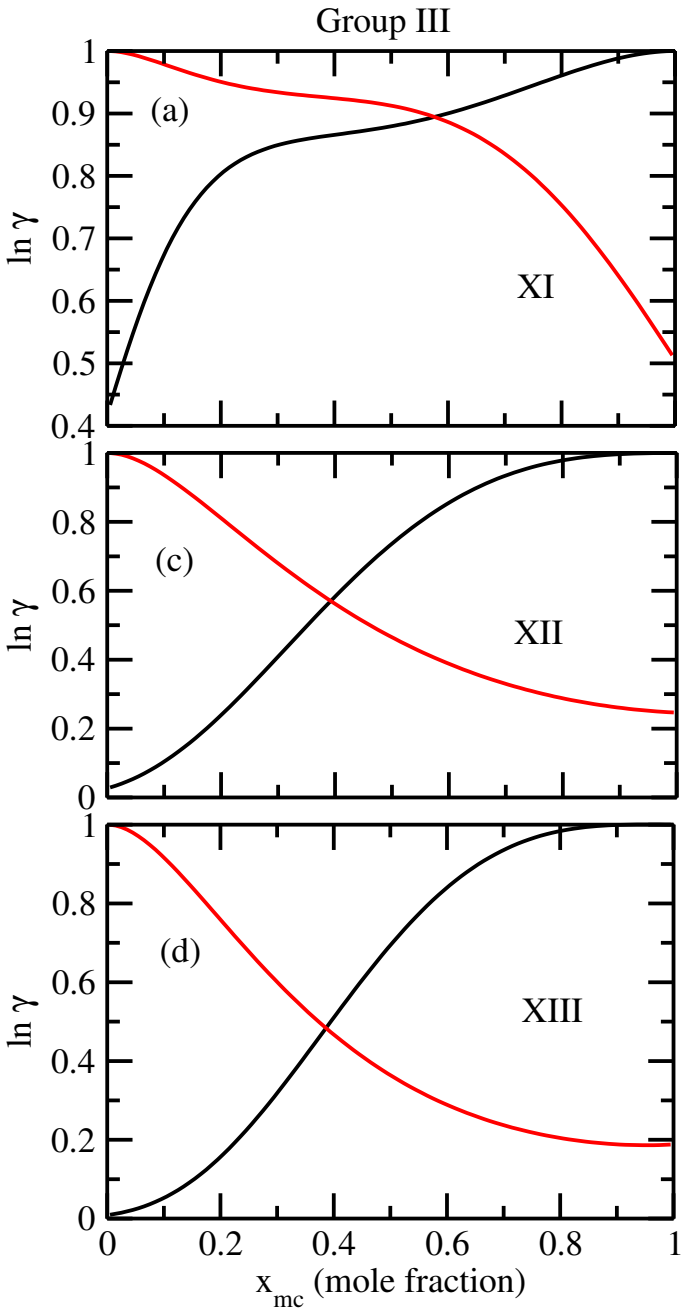
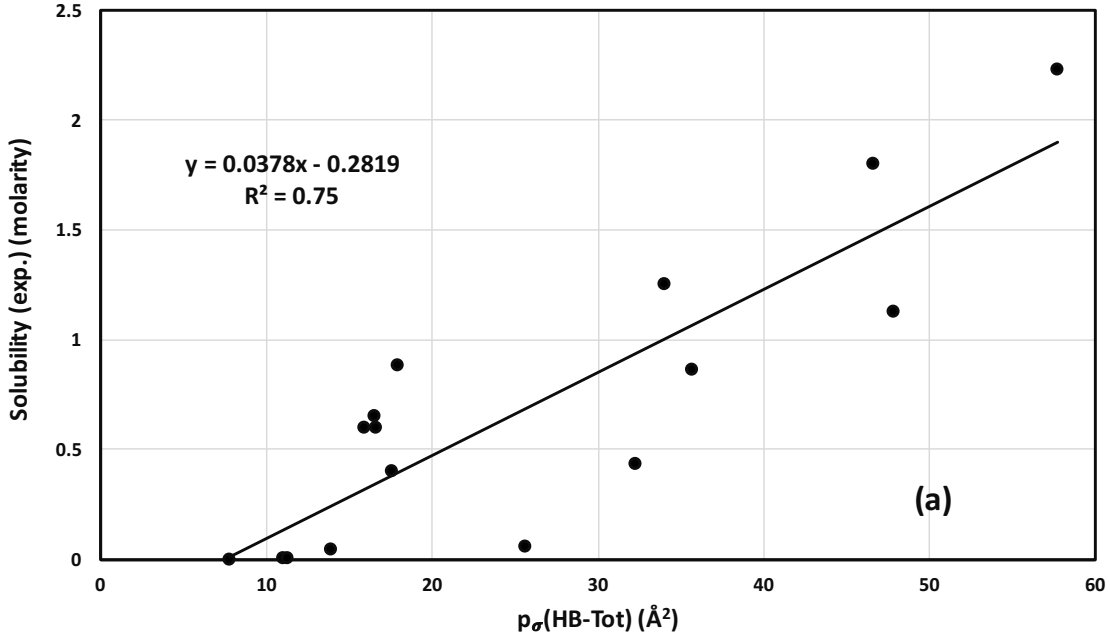


Figure. S 8: Gibbs-Duhem relationship of Group III type of metal complexes in acetonitrile solvent. The black curve is for the solute and the red curve is for the solvent.



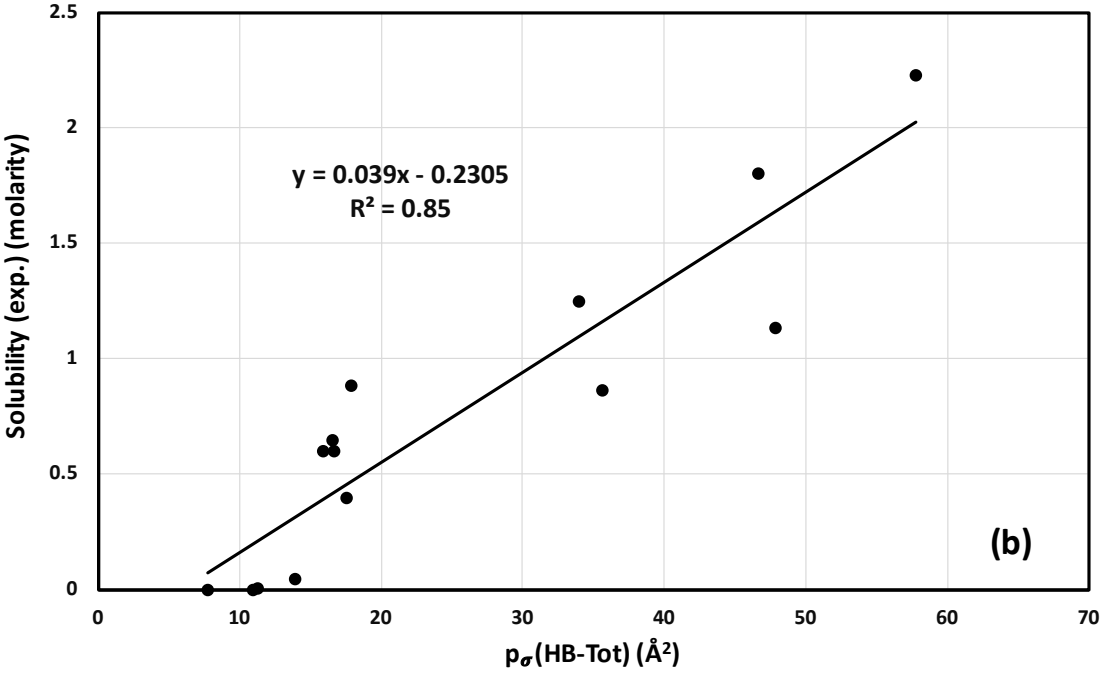


Figure. S 9: The experimental solubility vs p_σ(HB-Tot) for (a) 16 different metal complexes and for (b) 14 different metal complexes for COSMOSAC-LANL model. The solubility is in molarity.

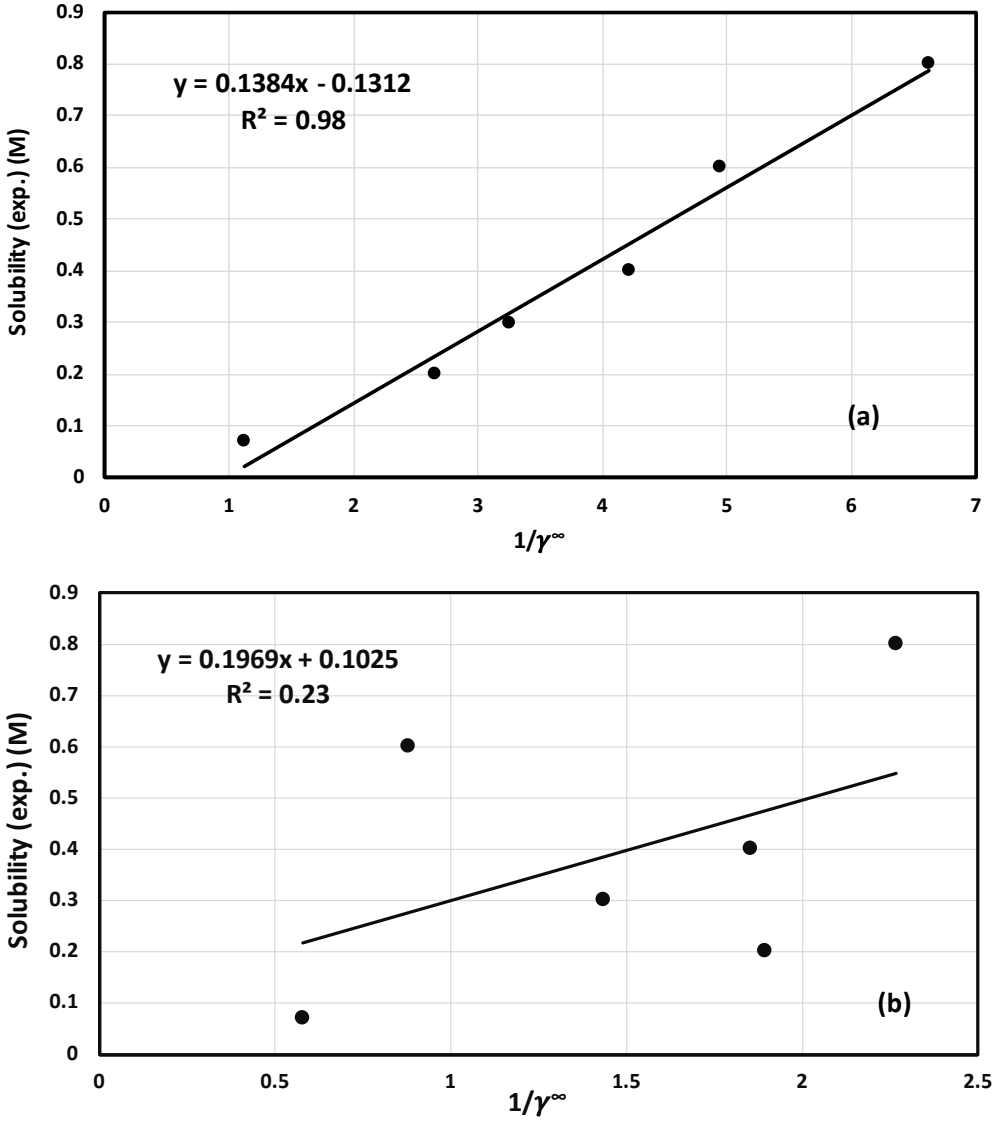


Figure. S 10: In fig. (a) and (b), the experimental solubility has been plotted as a function of $1/\gamma_{i/S}^{\infty}$ for the COSMOSAC-LANL and COSMOSAC-2013 model, respectively. These results have been shown for a particular metal complex $V(acac)_3$ in 6 different organic solvents. The solubility is in molarity unit.

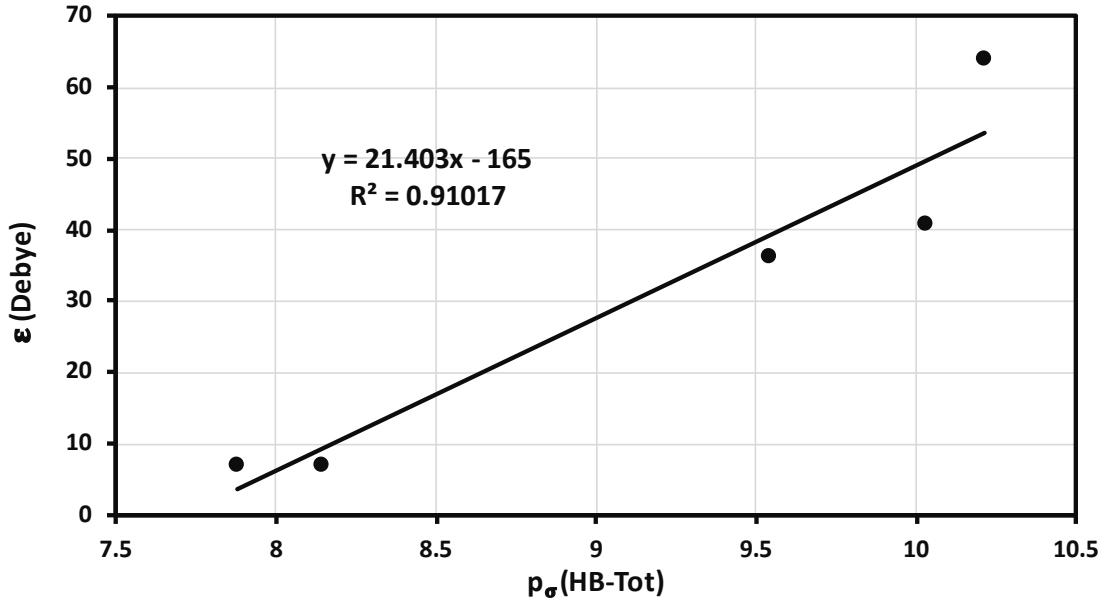


Figure. S 11: ε vs p_σ(HB-Tot) for 1,3do, MA, DMPU, GBL and PC solvents.

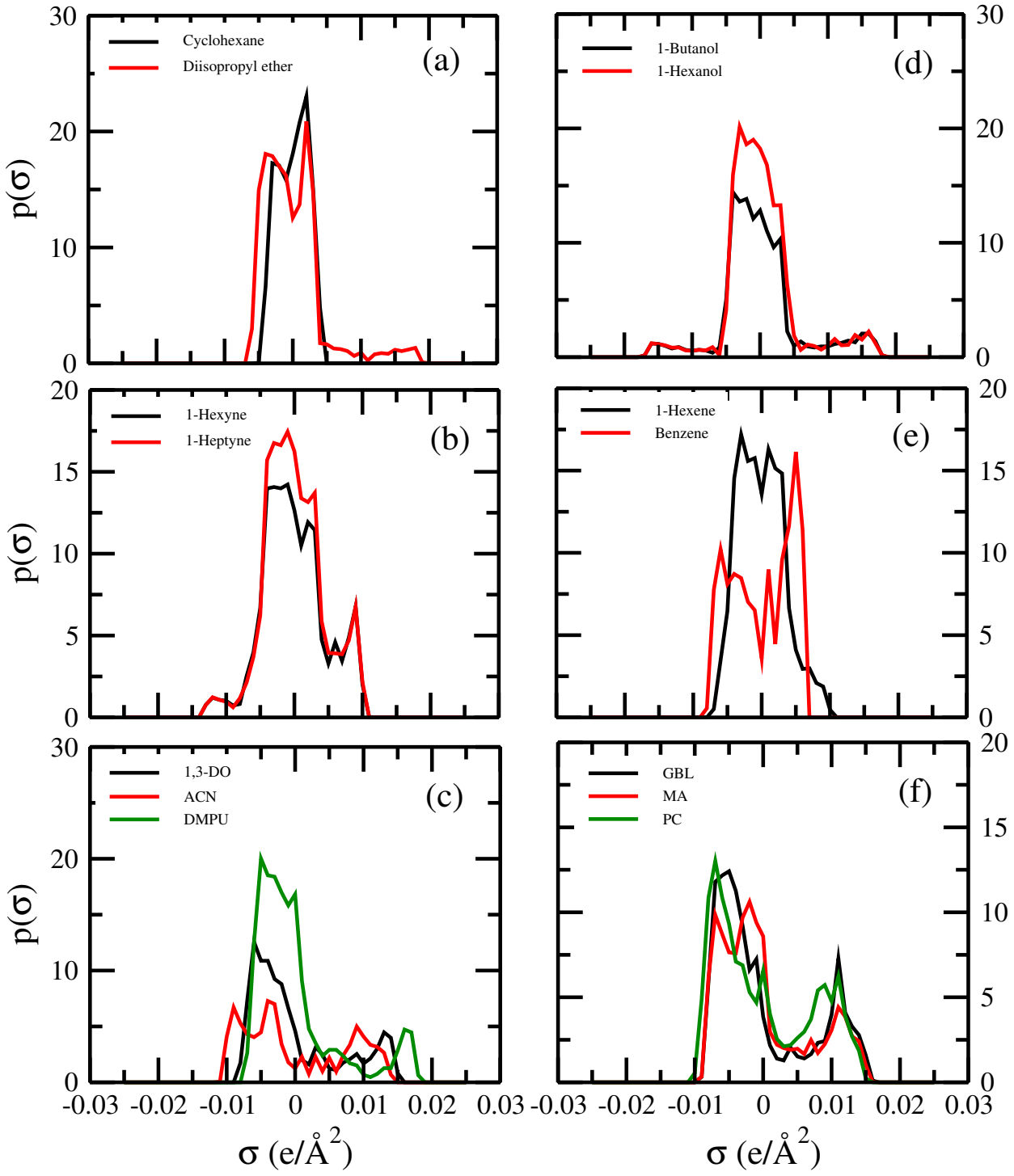


Figure. S 12: Total σ profile of 14 different organic solvents.

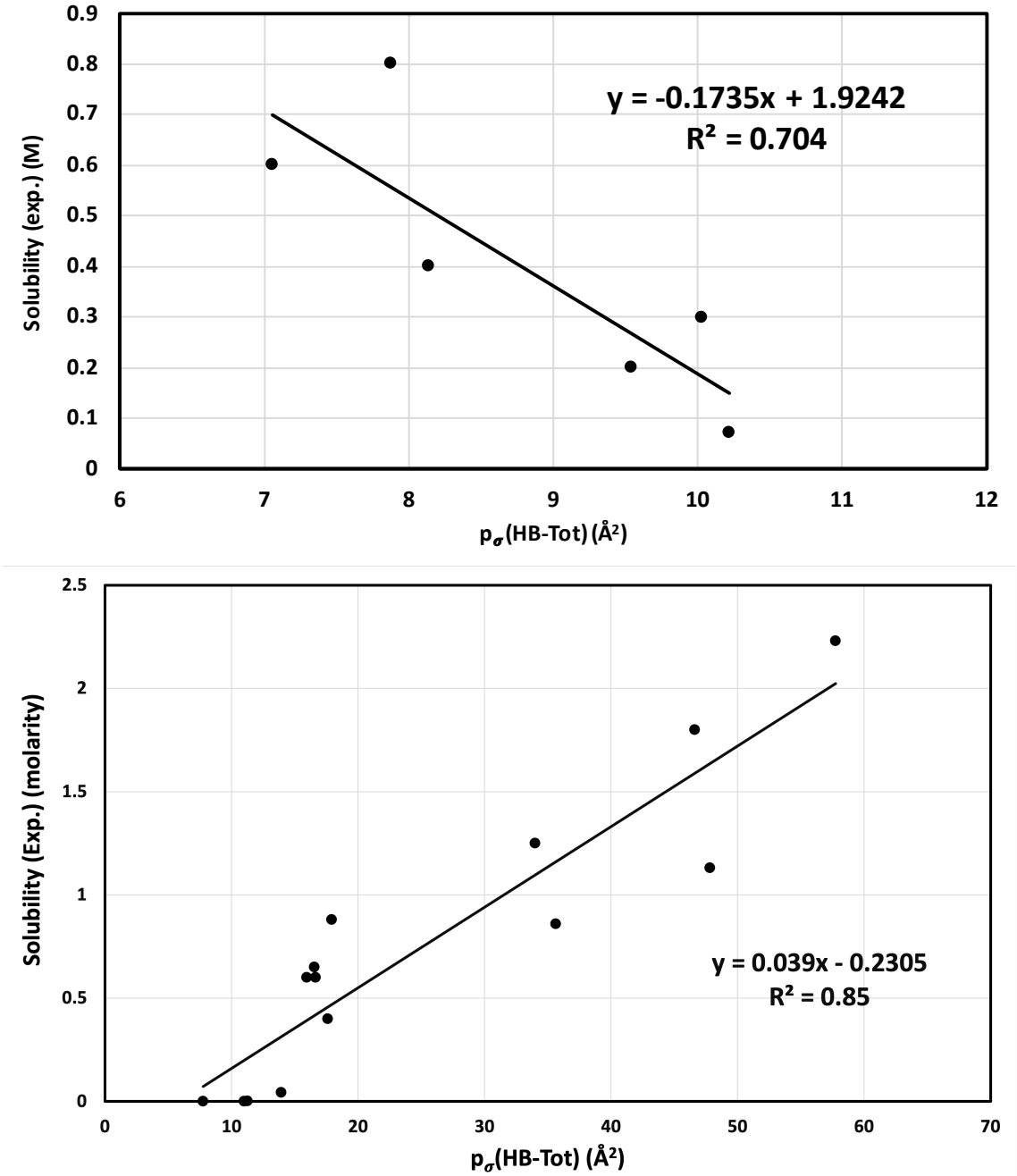


Figure. S 13: The experimental solubility vs p_σ(HB) for (top) V(acac)$_3$ in 6 different organic solvents and (bottom) 14 different metal complexes in acetonitrile solvent, respectively. These two plots correspond to the 14×6 (84) screening model.

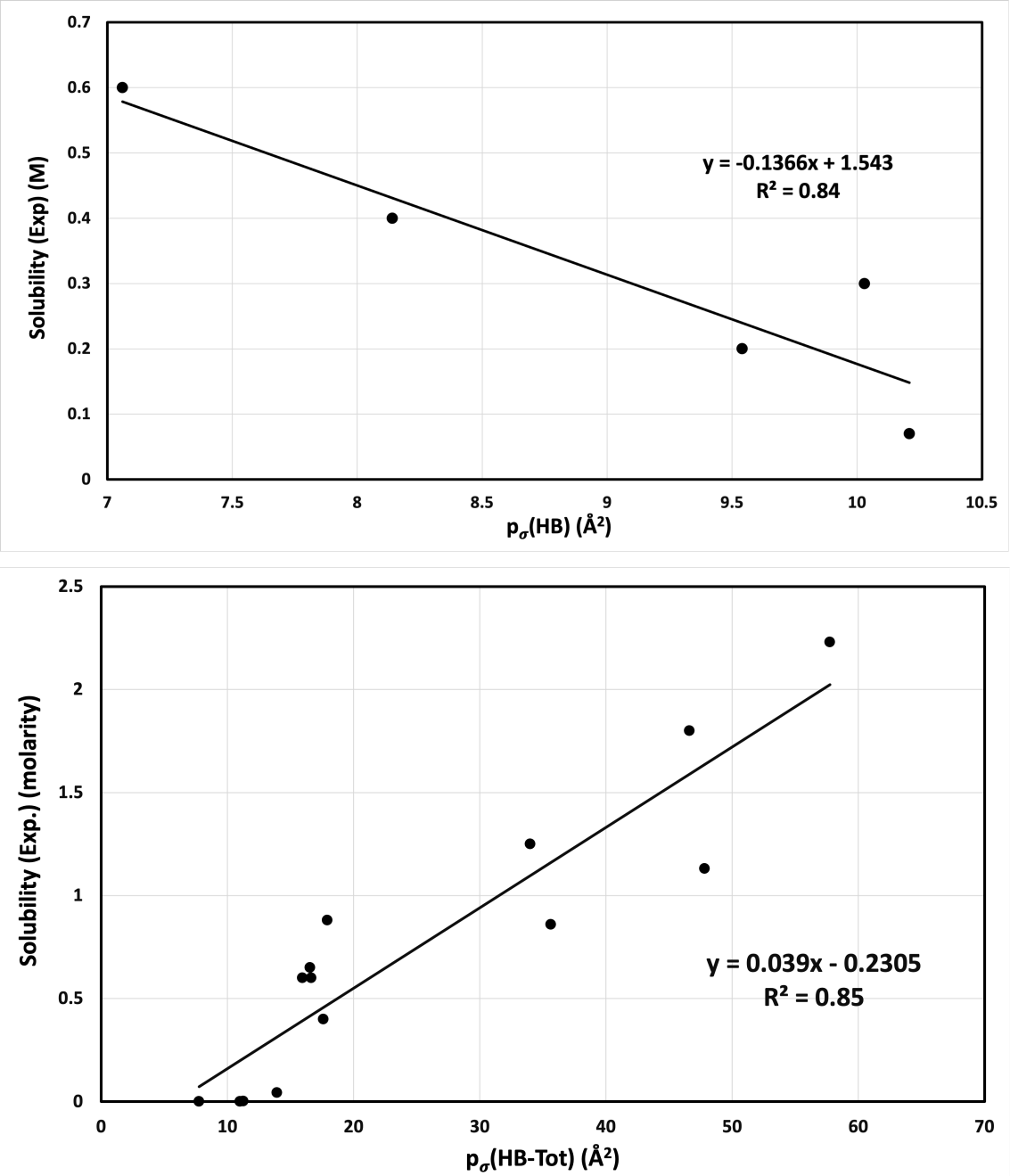


Figure. S 14: The experimental solubility vs p_σ(HB) for (top) $V(acac)_3$ in 5 different organic solvents and (bottom) 14 different metal complexes in acetonitrile solvent, respectively. These two plots correspond to the 14×5 (70) screening model.

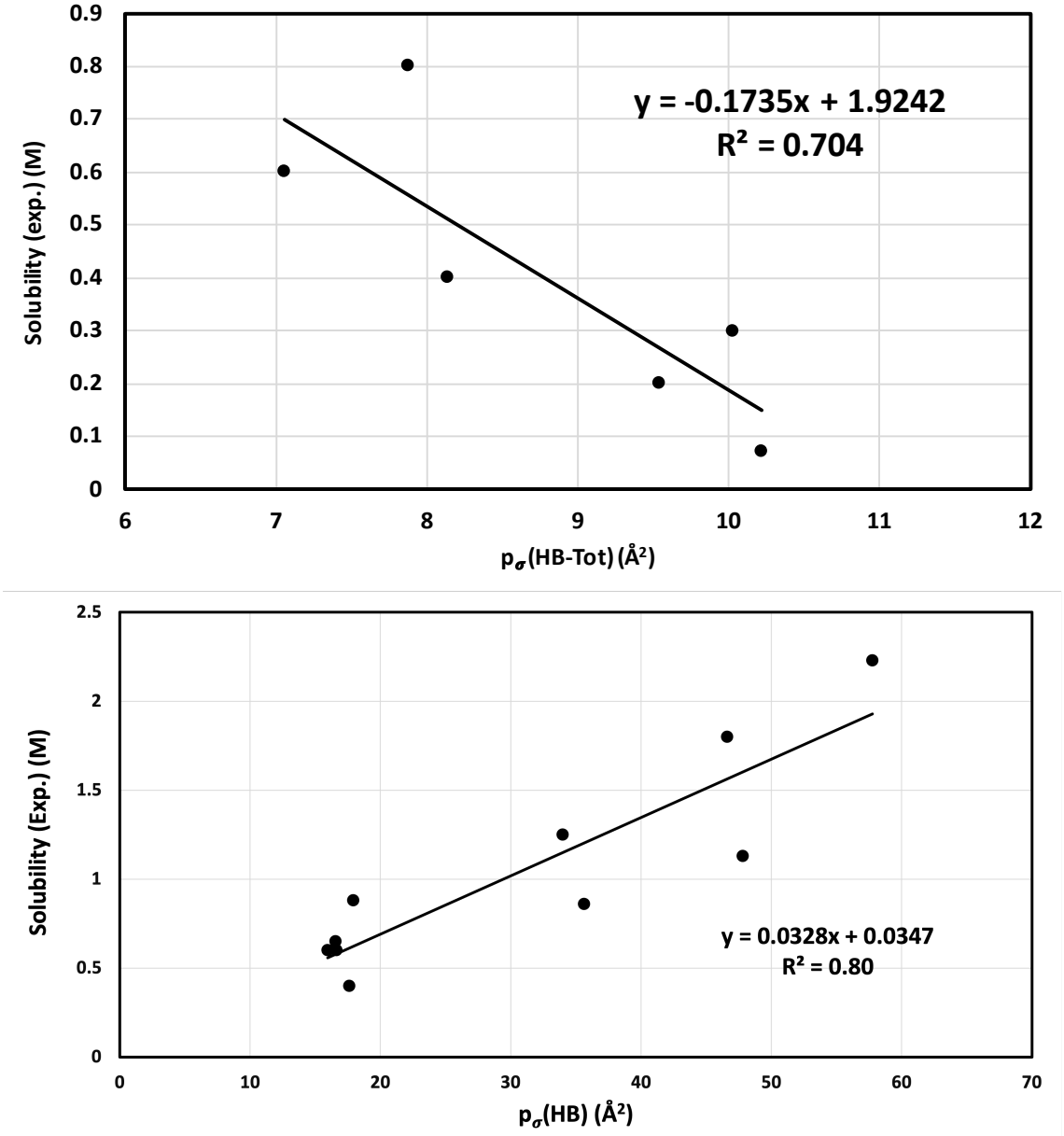


Figure. S 15: The experimental solubility vs p_σ(HB) for (top) V(acac)$_3$ in 6 different organic solvents and (bottom) 10 different metal complexes in acetonitrile solvent, respectively. These two plots correspond to the 10×6 (60) screening model.

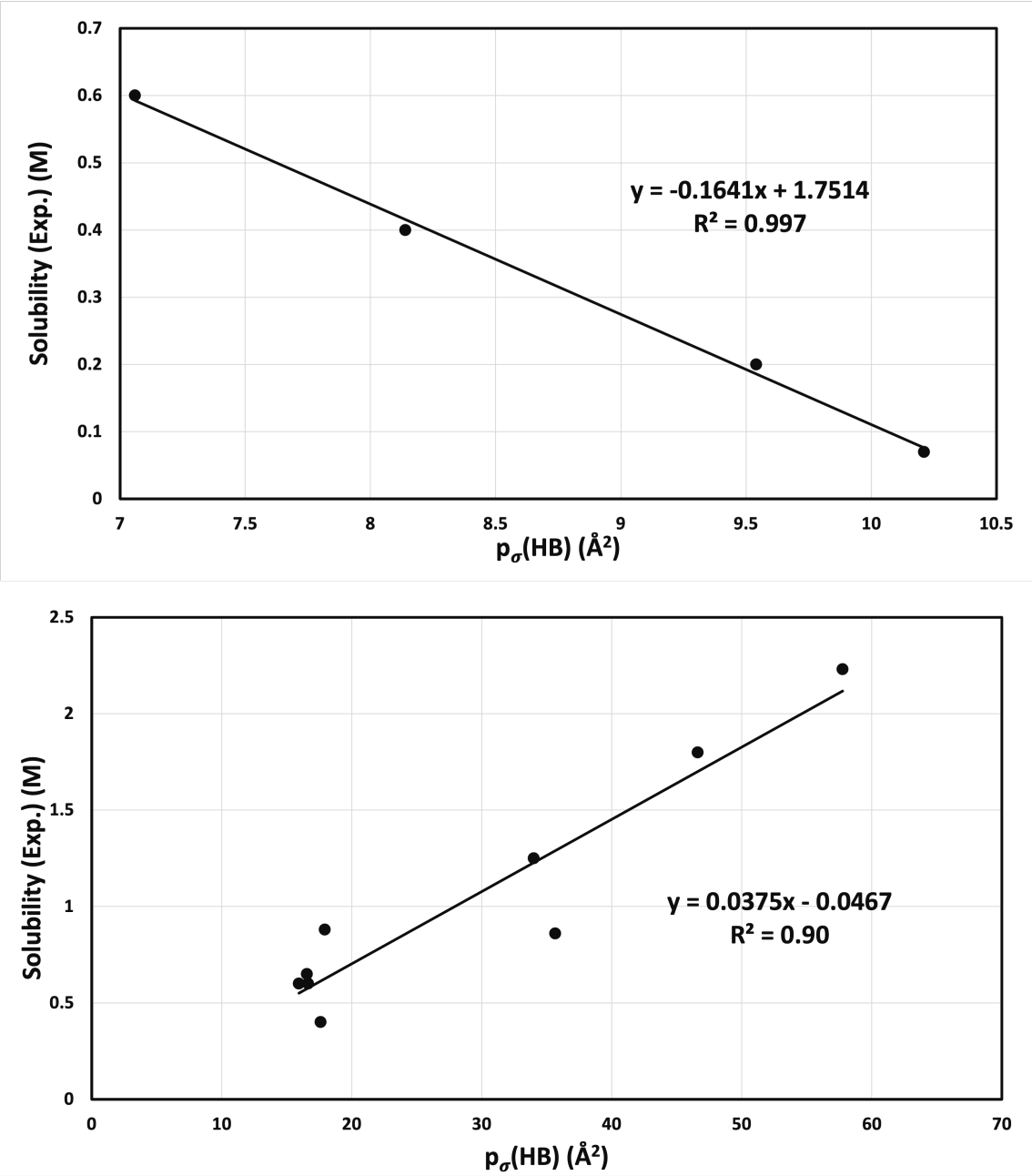


Figure. S 16: The experimental solubility vs p_σ(HB) for (top) V(acac)$_3$ in 4 different organic solvents and (bottom) 9 different metal complexes in acetonitrile solvent, respectively. These two plots correspond to the 9×4 (36) screening model.

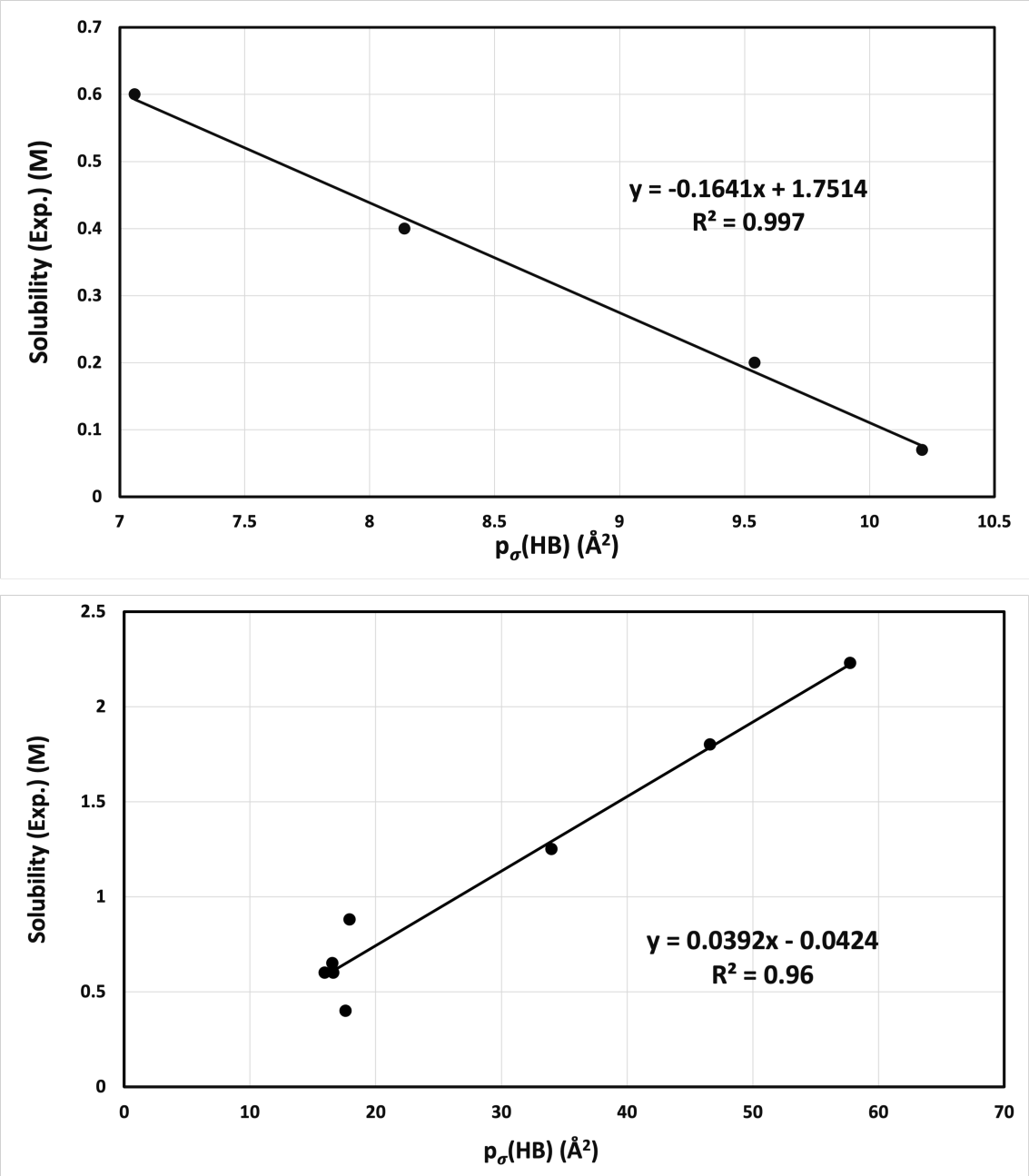


Figure. S 17: The experimental solubility vs p_σ(HB) for (top) V(acac)$_3$ in 4 different organic solvents and (bottom) 8 different metal complexes in acetonitrile solvent, respectively. These two plots correspond to the 8×4 (32) screening model.

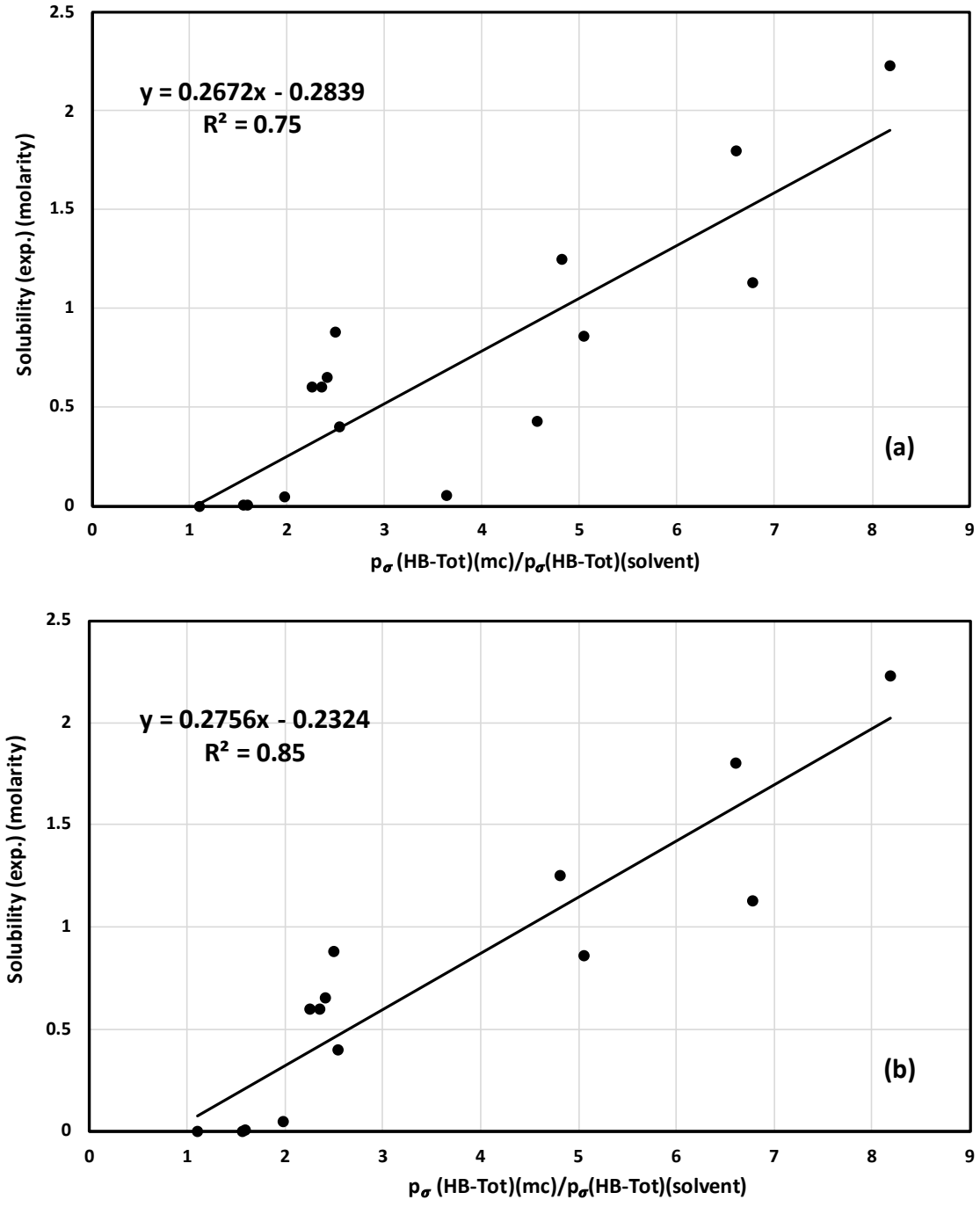


Figure. S 18: The experimental solubility vs χ for (a) 16 different metal complexes and (b) 14 different metal complexes, respectively. The definition of χ has been given in section 6 in the main manuscript.

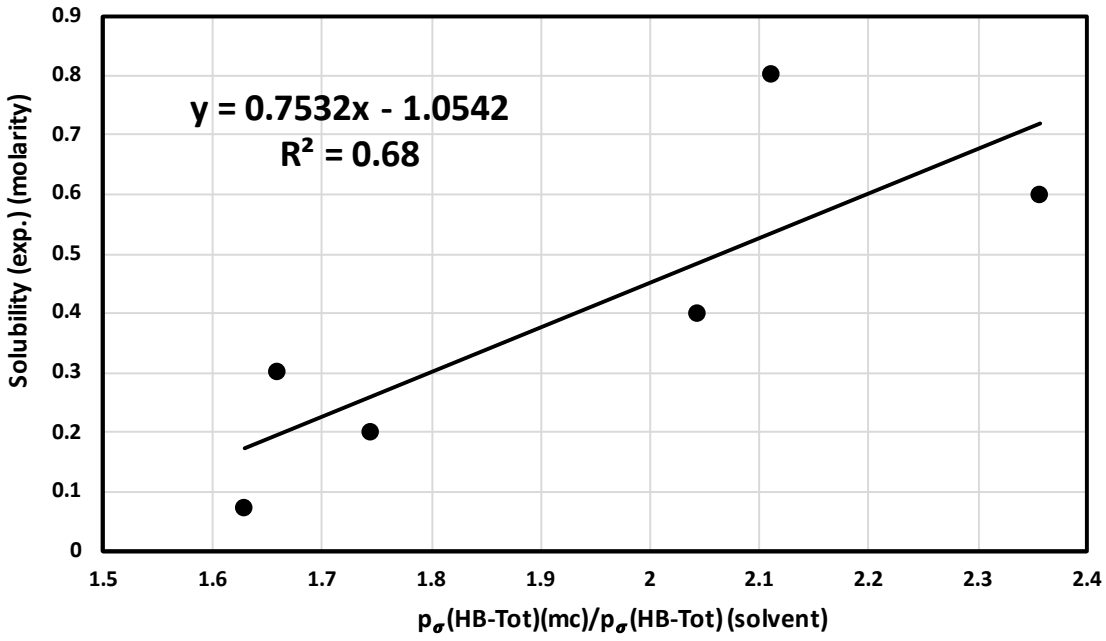


Figure. S 19: The experimental solubility vs χ for V(acac)$_3$ in 6 different organic solvents. The definition of χ has been given in section 6 in the main manuscript.