Supporting materials for MJ_1 and MJ_2

The MJ_1 molecule

Coordinates

Energy: -443898.1076954

C	-2.83740	-1.48550	0.47639
C	-4.20161	-1.26276	0.40403
C	-4.66481	-0.00892	-0.01739
C	-1.91114	-0.48257	0.13338
C	-2.39662	0.78530	-0.28738
C	-3.77895	1.00252	-0.35717
C	-0.49048	-0.75553	0.21786
N	0.39619	0.12068	-0.10458
C	1.76606	-0.17585	-0.08068
C	2.29622	-1.42042	-0.44540
C	3.66914	-1.65042	-0.44546
C	2.66009	0.85919	0.26441
C	4.53913	-0.62525	-0.08230
C	4.03371	0.62452	0.27027
H	-0.20410	-1.74800	0.58608
H	-2.45970	-2.45031	0.80090
H	-5.73140	0.17807	-0.07786
H	-4.12906	1.97537	-0.68047
H	1.61858	-2.20261	-0.76804
H	4.70983	1.42737	0.55002
H	4.05563	-2.61770	-0.74349
H	5.61039	-0.78897	-0.08207
O	-1.57346	1.78934	-0.61739
O	2.11996	2.06543	0.60355
H	-0.63942	1.46943	-0.50410
H	2.82542	2.69411	0.78924
H	-4.90150	-2.04556	0.66922

Electronic spectra

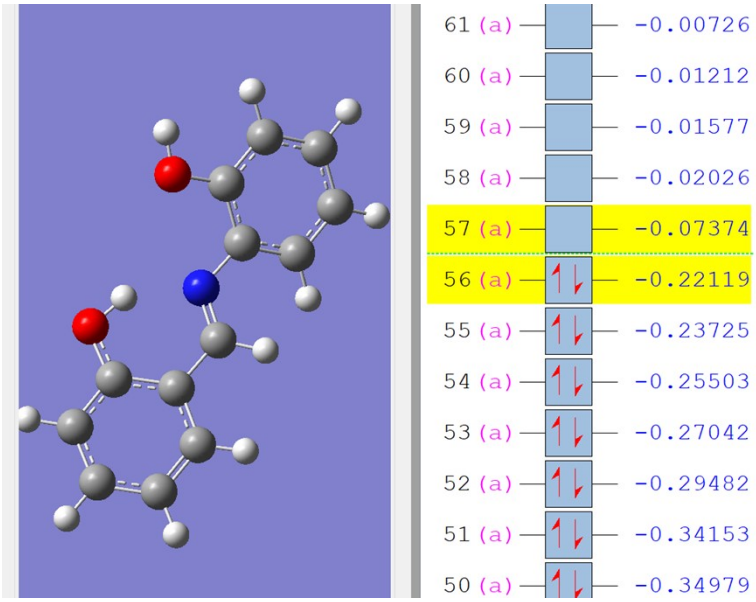

Figure S1:orbital diagram for MJ_1

Excited State 1: Singlet-A 3.5285 eV 351.38 nm f=0.4059 <S**2>=0.000

56 -> 57 0.69133

Excited State 4: Singlet-A 4.5598 eV 271.91 nm f=0.2636 <S**2>=0.000

52 -> 57 0.22089

53 -> 57 0.52575

54 -> 57 0.33135

56 -> 57 -0.12166

56 -> 58 0.10893

56 -> 60 0.14540

MJ_1-Cu^{2+} complex

Coordinate

C	-2.83307	-2.34902	-0.42527
C	-4.18708	-2.10680	-0.40764
C	-1.89520	-1.34025	-0.05594
C	-4.67345	-0.82742	-0.02439
C	-2.39971	-0.05370	0.37729
C	-3.80647	0.17779	0.33457
C	-0.51240	-1.62487	-0.16697
N	0.46717	-0.75435	0.03216
C	1.81750	-1.03622	0.07501

C	2.42710	-2.31037	0.07468
C	3.80089	-2.40094	-0.05282
C	2.63771	0.15180	0.08365
C	4.03835	0.02550	-0.12365
C	4.60270	-1.23092	-0.16233
H	1.82807	-3.20754	0.14524
H	4.62792	0.92810	-0.17773
H	4.27367	-3.37245	-0.08585
H	5.67387	-1.33560	-0.26656
H	-2.45778	-3.31529	-0.73879
H	-4.88293	-2.88004	-0.70026
H	-5.73928	-0.64346	-0.02345
H	-4.14958	1.15780	0.62979
O	-1.61972	0.89437	0.84497
O	2.07210	1.30650	0.36264
Cu	0.14209	1.25593	0.21339
H	-0.25098	-2.63180	-0.48702
Cl	-0.23730	3.30026	-0.67805

TDDFT-electronic spectra

406

Table S1: The transition, oscillator strength and molecular orbitals involved in the transitions for the MJ_1-CuCl comples

Band(nm)	**Transition**		**Oscillator strength**
406.28	64 -> 74 66 -> 74 HOMO-6 to LUMO 67 -> 74 71 -> 75 73 -> 75 HOMO to LUMO +1	-0.18375 0.28768 0.10026 0.16339 0.54026	0.1280
491.09	62 -> 74 63 -> 74 64 -> 74 65 -> 74 67 -> 74 HOMO-6 to LUMO 68 -> 74 69 -> 74 73 -> 74	-0.23022 0.12067 0.12860 0.19019 0.43434 -0.31312 -0.14509 0.19064	0.0948
542.09	67 -> 74 HOMO-6 to LUMO 68 -> 74 HOMO-5 to LUMO 69 -> 74 70 -> 74 71 -> 74 72 -> 74 73 -> 75	0.33980 0.34228 0.28524 0.21342 -0.16043 0.12127 -0.24609	0.0478
770.50	64 -> 74	-0.10467	0.0196

	68 -> 74 69 -> 74 70 -> 74 HOMO-3 to LUMO 71 -> 74 HOMO-2 to LUMO 73 -> 74 HOMO to LUMO 73 <- 74	-0.19428 -0.10531 0.49781 0.22171 -0.36222 0.10931	
870.21	67 -> 74 68 -> 74 70 -> 74 71 -> 74 72 -> 74 HOMO-1 to LUMO 73 -> 74 HOMO to LUMO	-0.26249 -0.18961 0.29711 -0.26240 0.32321 0.35646	0.0434

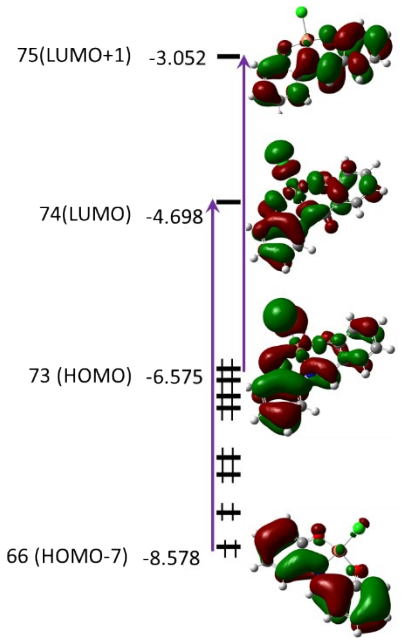

Figure S2: the HOMO to LUMO +1 and HOMO-7 to LUMO transition responsible for the 406.28 nm and in the MJ_1-CuCl complex

491 band

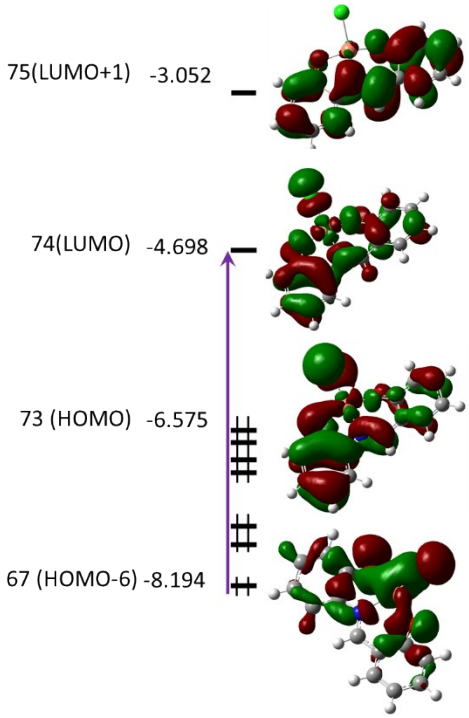

Figure S3: the HOMO-6 to LUMO transition responsible for the 491.09 nm band in the MJ_1-CuCl complex

542 band

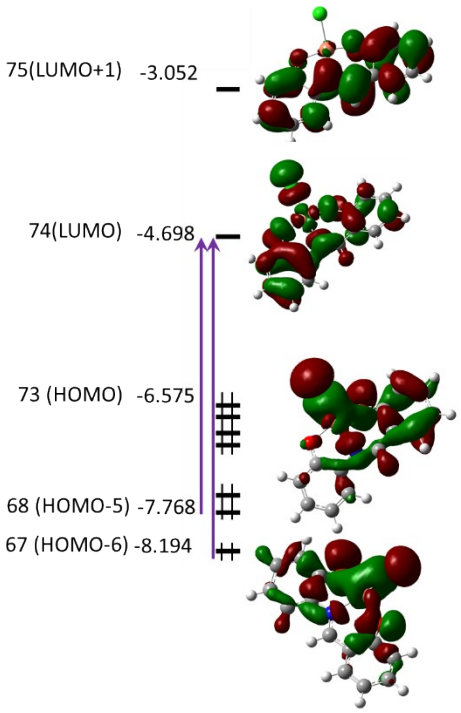

Figure S4: the HOMO to LUMO +1 and HOMO-7 to LUMO transition responsible for the 542.09 nm band in the MJ_1-CuCl complex

770 band

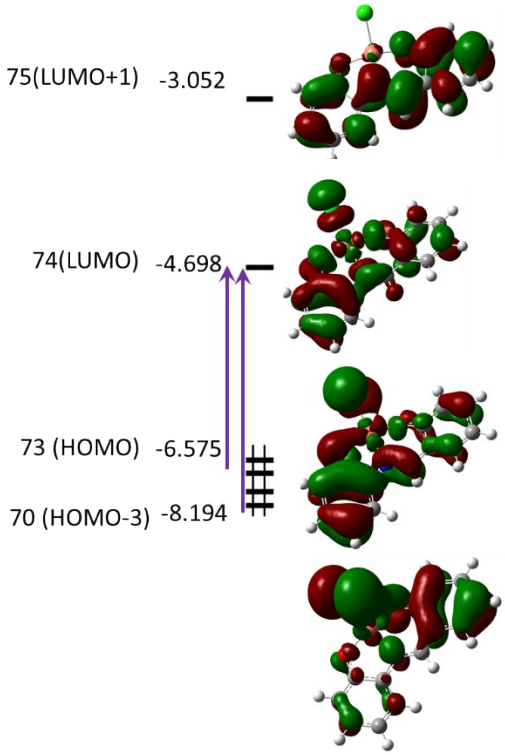

Figure S5: the HOMO to LUMO and HOMO-3 to LUMO transition responsible for the 770.50 nm band in the MJ_1-CuCl complex

870 band

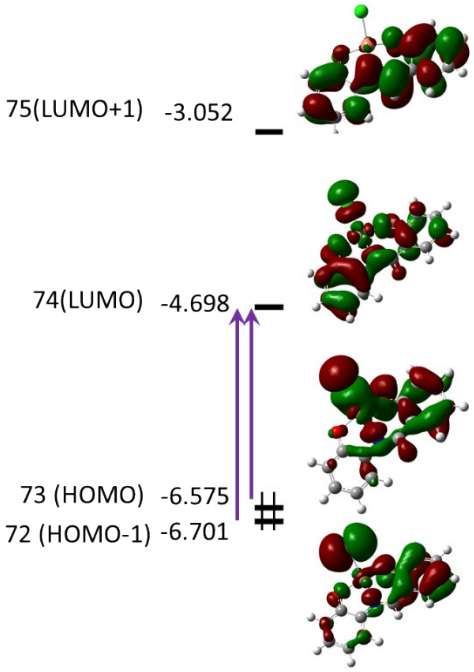

Figure S6: the HOMO to LUMO and HOMO-1 to LUMO transition responsible for the 870.21 nm band in the MJ_1-CuCl complex

MJ_2 molecule

Coordinates

C	1.74439	-0.49468	0.08767
C	2.99581	0.08183	-0.00918
C	3.12931	1.44905	-0.27088
C	0.58571	0.28662	-0.07892
C	0.71750	1.67663	-0.33949
C	1.99906	2.23539	-0.43233
C	-0.71828	-0.34179	0.02588
N	-1.80621	0.32462	-0.13925
C	-3.06531	-0.29057	-0.09756
C	-3.31677	-1.57887	-0.58718
C	-4.59646	-2.12514	-0.55884
C	-4.14758	0.46146	0.40504
C	-5.65236	-1.37946	-0.03958
C	-5.42669	-0.09082	0.43921
H	1.64289	-1.55432	0.29112
H	4.11353	1.89392	-0.34535
H	2.08543	3.29647	-0.63183
H	-2.50145	-2.13980	-1.02934
H	-6.24910	0.49458	0.84003
H	-4.76956	-3.11869	-0.95449
H	-6.65439	-1.79141	-0.01540
O	-0.34270	2.47789	-0.49450
O	-3.87687	1.71742	0.86295
Br	4.56653	-0.99733	0.21647
H	-0.73076	-1.41074	0.26850
H	-4.69268	2.13937	1.15265
H	-1.16219	1.92443	-0.38814

Electronic spectra

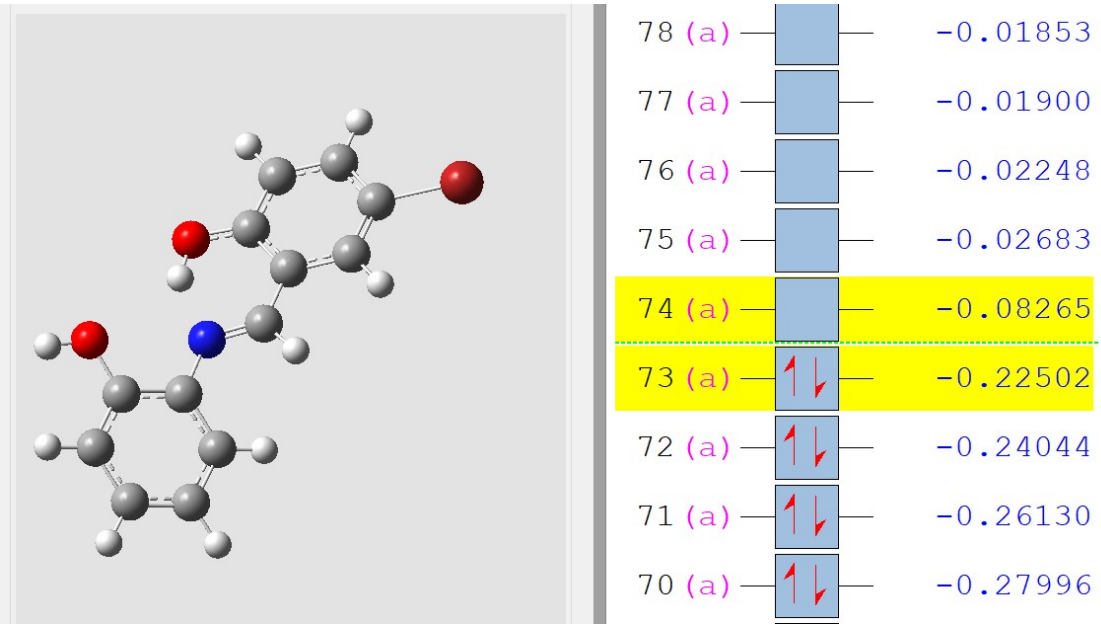

Figure S7: orbital diagram for MJ_2

Excited State 1: Singlet-A 3.4020 eV 364.44 nm f=0.3453 <S**2>=0.000

73 -> 74 0.69581

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -3280.81563895

Excited State 4: Singlet-A 4.5666 eV 271.50 nm f=0.2480 <S**2>=0.000

67 -> 74 0.13220

68 -> 74 0.20576

70 -> 74 0.53712

71 -> 74 0.26915

73 -> 75 0.18862

73 -> 76 -0.12106

MJ_2-Cu^{2+} complex

Coordinate

C	-2.38765	-0.87721	-0.02392
C	-3.52844	-0.11955	0.04849
C	-1.11159	-0.28961	0.21455
C	-3.47019	1.26467	0.34656

C	-1.04592	1.11183	0.56819
C	-2.25697	1.86709	0.57579
C	0.04087	-1.10015	0.05429
N	1.29100	-0.67068	0.13624
C	2.42793	-1.45261	0.12332
C	2.49866	-2.86229	0.18007
C	3.71749	-3.48483	-0.01435
C	3.64037	-0.67754	0.00090
C	4.86437	-1.34774	-0.27193
C	4.89709	-2.72456	-0.25036
H	1.60842	-3.45262	0.34610
H	5.74935	-0.74845	-0.42291
H	3.77616	-4.56407	-0.00386
H	5.83371	-3.24223	-0.40477
H	-2.44487	-1.92656	-0.27675
H	-4.38324	1.83962	0.38498
H	-2.17958	2.91884	0.80584
O	0.06891	1.70674	0.91875
O	3.58729	0.61720	0.22520
Cu	1.78395	1.31918	0.17557
H	-0.13393	-2.14345	-0.20112
Cl	2.15246	3.29361	-0.86207
Br	-5.26158	-0.93344	-0.28796

Electronic spectra

Band(nm)	**Transition**		**Oscillator strength**
412.57	79 -> 91 80 -> 91 81 -> 91 84 -> 91 86 -> 92 87 -> 92 88 -> 92 89 -> 92 90 -> 92	0.16446 0.10276 -0.11555 -0.13940 -0.10789 0.14396 -0.13351 0.17443 0.55824	0.2054
495.59	77 -> 91 78 -> 91 79 -> 91 80 -> 91 84 -> 91 85 -> 91 86 -> 91 90 -> 91	-0.20337 0.16380 0.10158 0.18985 0.42750 -0.30711 -0.17185 -0.19599	0.0951
550.97	84 -> 91 85 -> 91 86 -> 91	0.30633 0.18989 0.50399	0.0397

	87 -> 91 88 -> 91 89 -> 91 90 -> 92	-0.12206 -0.13597 0.12104 0.21764	
770.38	79 -> 91 84 -> 91 85 -> 91 87 -> 91 88 -> 91 90 -> 91 90 <- 91	0.10800 -0.10150 0.19709 0.51753 -0.12108 -0.37592 0.11419	0.0213
873.71	84 -> 91 85 -> 91 87 -> 91 88 -> 91 89 -> 91 90 -> 91	-0.26061 -0.19650 -0.19734 -0.29027 0.41019 -0.30961	0.0576

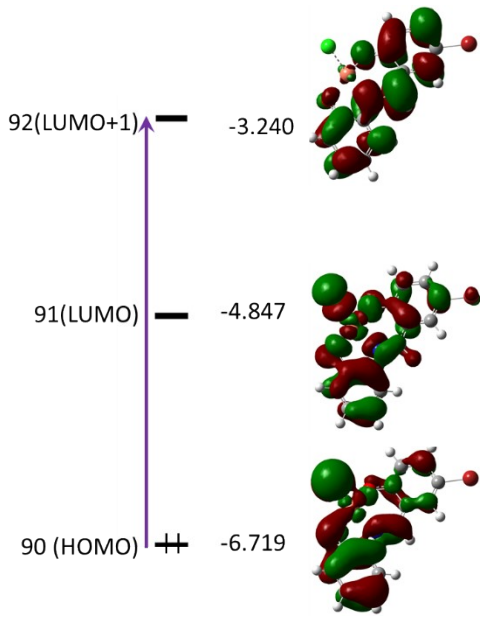

Figure S8: the HOMO to LUMO transition responsible for the 412.57 nm band in the MJ_2-CuCl complex

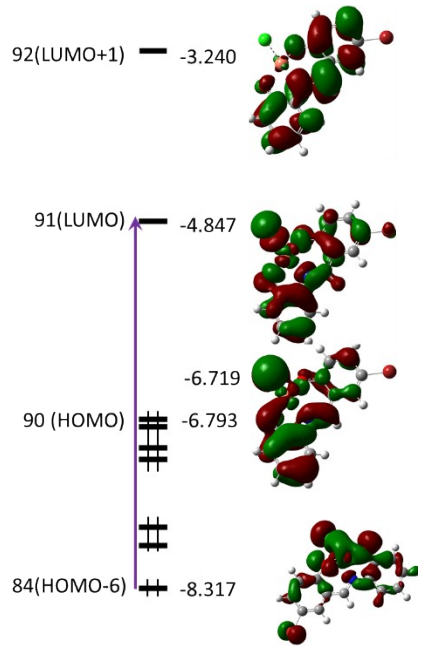

Figure S9: the HOMO-6 to LUMO transition responsible for the 495.59 nm band in the MJ_2-CuCl complex

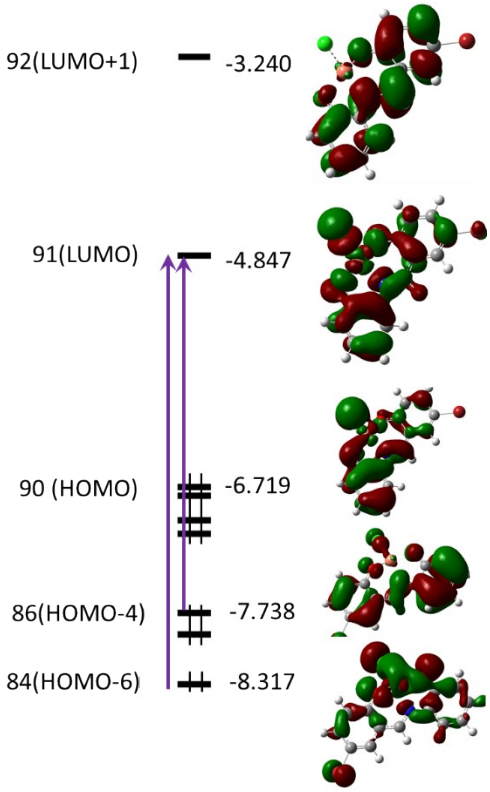

Figure S10: the HOMO-6 and HOMO-4 to LUMO transition responsible for the 770.38 nm band in the MJ_2-CuCl complex

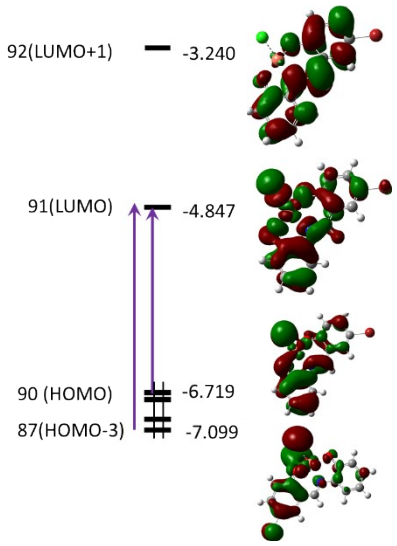

Figure S11: the HOMO and HOMO-3 to LUMO transition responsible for the 550.97 nm band in the MJ_2-CuCl complex

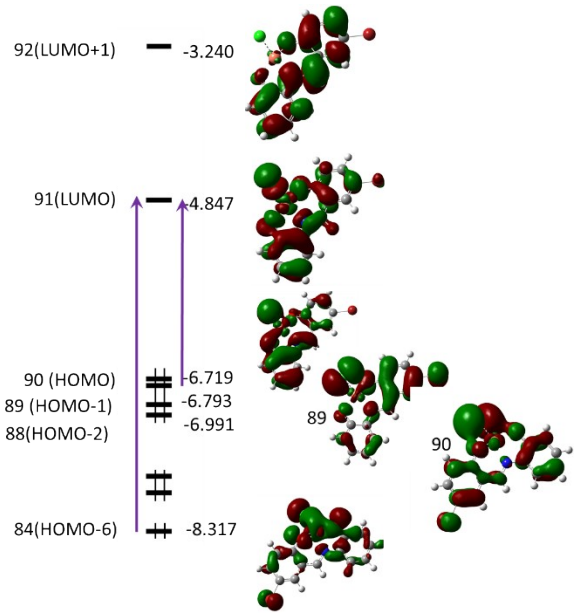

Figure S12: the HOMO-2 and HOMO-6 to LUMO transition responsible for the 873.71 nm band in the MJ_2-CuCl complex

Reactivity descriptors

Global reactivity descriptors like chemical hardness (η), electronic chemical potential (μ), electronegativity (χ), global softness (S) and electrophilicity index (ω), were also considered and calculated at the PBE1PBE/6-311g(d,p) level of theory. The chemical potential, μ, and chemical hardness, η, are defined as the first derivative of the electronic energy and chemical potential

with respect to the electron number (N) at constant external potential, $v(r)$, respectively as given in equations 1 and 2

$$\mu \frac{1}{2}\left[\frac{\partial E}{\partial N}\right]_v \quad (1)$$

$$\eta = \frac{1}{2}\left[\frac{\partial \mu}{\partial N}\right]_v = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_v \quad (2)$$

The chemical potential, μ characterizes the escaping tendency of electrons from the equilibrium system and the molecular hardness determines the resistance to charge transfer. Within the framework of finite differences approximation, the above descriptors and other global descriptors can also be calculated as follows [1–4]

	$I = -E_{HOMO}$	(3)
	$A = -E_{LUMO}$	(4)
	$\eta = -\frac{E_{HOMO} - E_{LUMO}}{2}$	(5)
	$\mu = \frac{E_{HOMO} + E_{LUMO}}{2}$	(6)
	$\omega = \frac{\mu^2}{2\eta}$	(7)
	$\chi = -\mu = -\frac{E_{HOMO} + E_{LUMO}}{2}$	(8)
	$S = 1/2\eta$	(9)
	$\omega^- = \frac{(\mu^-)^2}{2\eta}$	
	$\omega^+ = \frac{(\mu^+)^2}{2\eta}$	

References

1. R. G. Pearson, Proc. Natl. Acad. Sci., 1986, 83, 8440-8441.
2. R. G. Pearson, J. Chem. Educ., 1987, 64, 561.
3. J. L. Reed, J. Phys. Chem. A., 1997, *101*, 7396-7400.
4. R. G. Parr, L. V. Szentpály and S. Liu, J. Am. Chem. Soc., 1999, 121, 1922-1924.