Supporting Information

Charge Transfer or J-Coupling? Assignment of an Unexpected Red-Shifted Absorption Band in a Metal-Organic Framework

Brian D. McCarthy, Eric R. Hontz, Shane R. Yost, Troy Van Voorhis, and Mircea Dincă

mdinca@mit.edu; tvan@mit.edu

Table of Contents **Page Number**

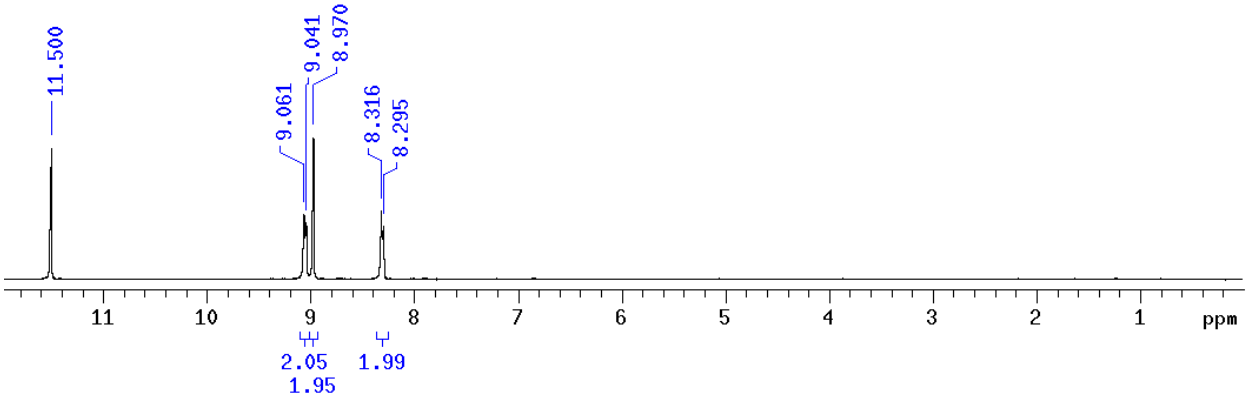


Figure S1. ^{1}H NMR spectrum of DPNI in deuterated trifluoroacetic acid (TFA-d). The spectrum was referenced to the proteo-TFA peak at 11.5 ppm.

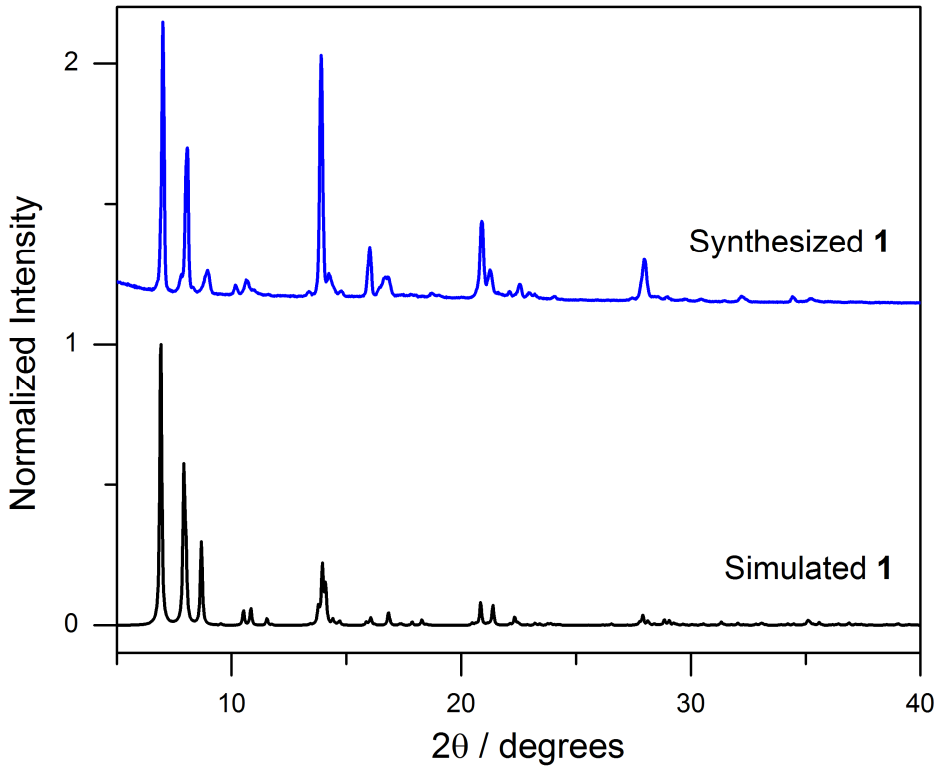


Figure S2. PXRD pattern of as synthesized **1** compared to the simulated pattern. The discrepancy of intensities at low angles of the as synthesized material with the simulated pattern is attributed to preferential orientation.

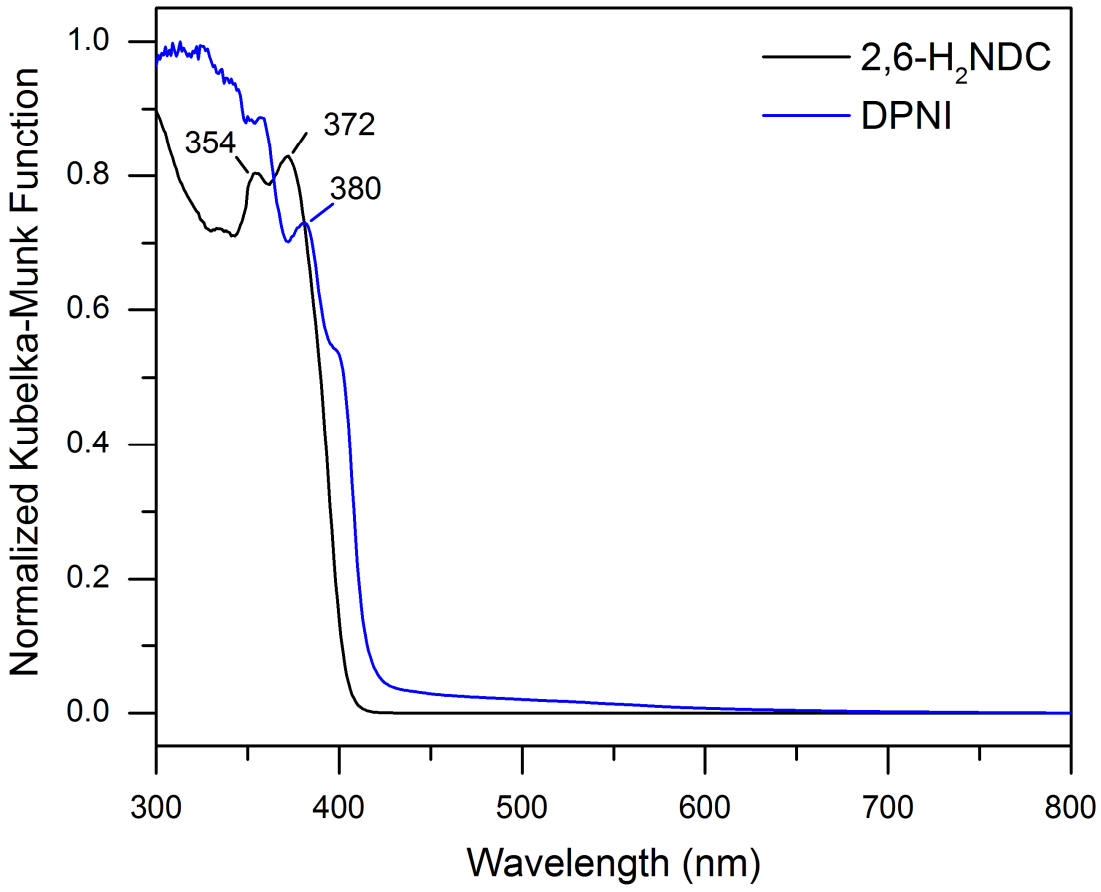


Figure S3. Diffuse reflectance spectra of solid 2,6-H_2NDC and DPNI.

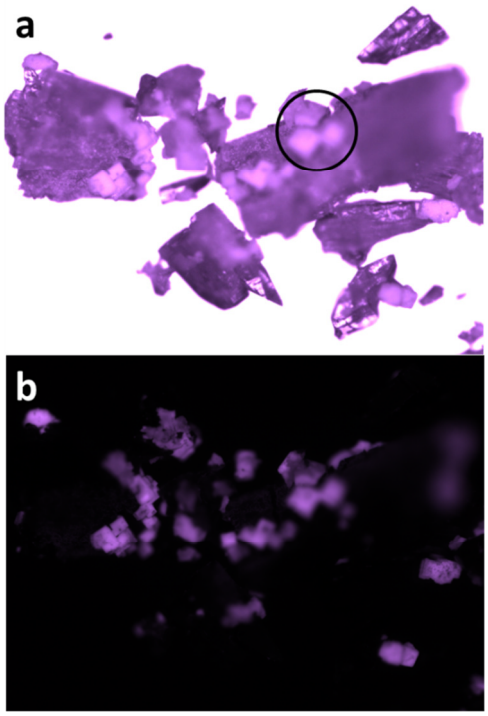


Figure S4. a) A false color bright field micrograph of **1** and an unidentified colorless second phase (one cluster identified by the black circle), and b) a false color epifluorescence micrograph of the same crystals under UV excitation.

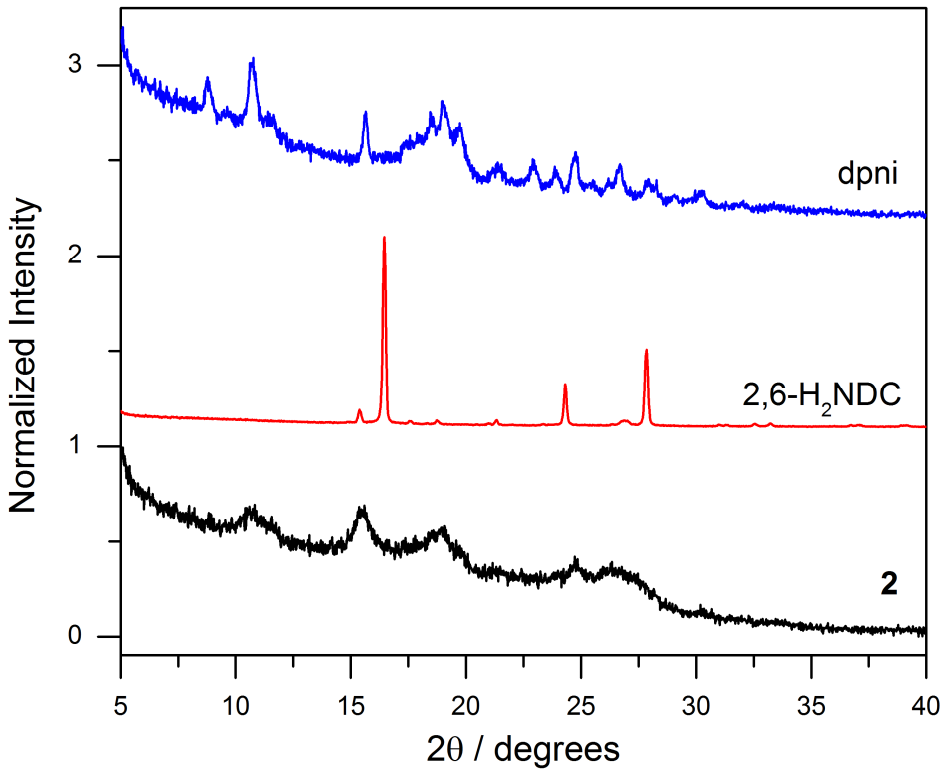


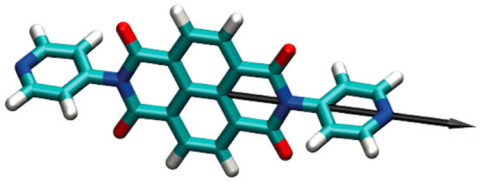
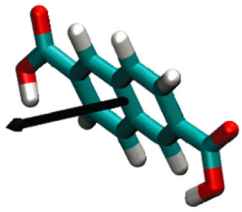
Figure S5. PXRD patterns of DPNI, 2,6-H_2NDC, and CT complex **2**.

Table S1. Effect of dielectric constant on CT energy for π-stacked DPNI/2,6-NDC^{2-} model system (cc-PVTZ).

ε	$S_0 \rightarrow$ CT (eV)	$S_0 \rightarrow$ CT range (nm)[a]
2	3.41	344 – 386
2.5	3.30	354 – 400
3	3.23	362 – 410
3.5	3.18	367 – 416
4	3.13	373 – 424
4.5	3.10	376 – 428

[a] Given 0.2 eV error bars

Table S2. Primary transition moment dipoles, transition energies, and oscillator strengths for studied ligands.

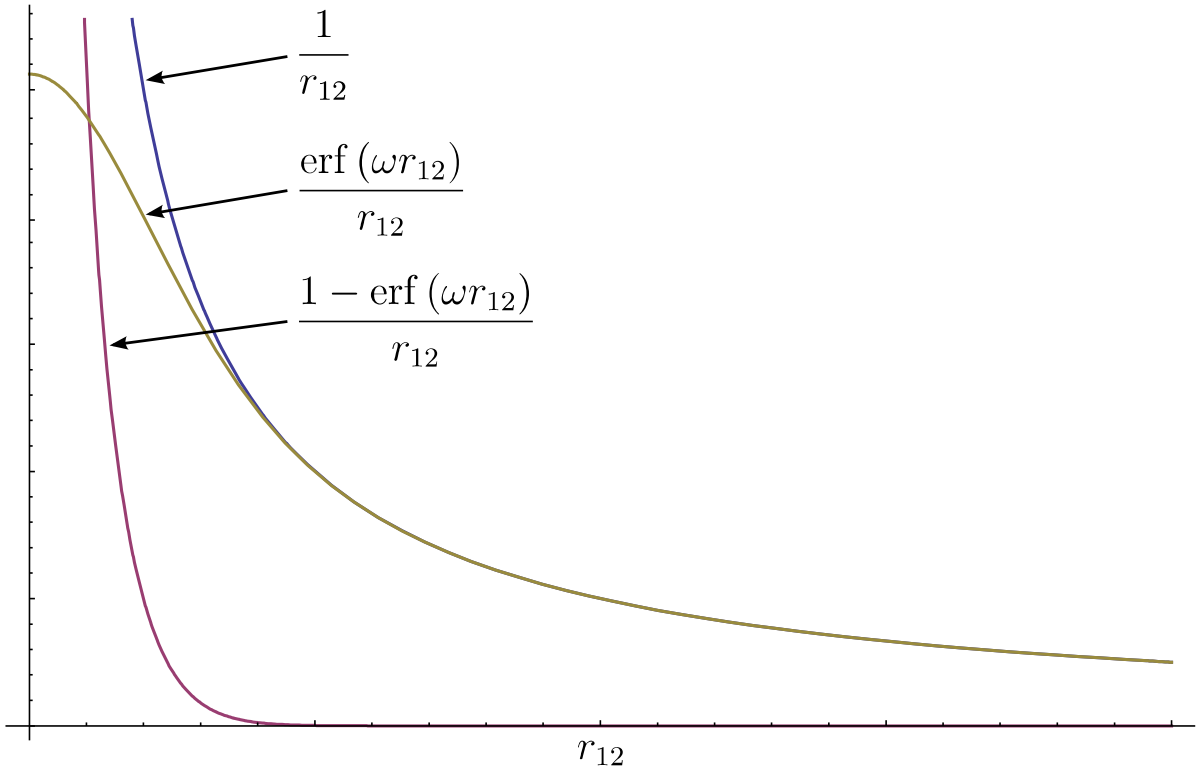
Organic moiety	primary transition moment dipole	$S_0 \rightarrow S_1$ (nm)[a]	oscillator strength
DPNI		313 – 349	0.4941
2,6-H_2NDC		301 – 334	0.0528

[a] Given 0.2 eV error bars

Customizing a long-range corrected hybrid function

A long-range-corrected (LRC) hybrid functional[1] splits the Coulomb repulsion term into short-range and long-range parts and calculates the short-range correlation energy using both generalized gradient approximations (GGAs) and Hartree-Fock (HF) and the long-range correlation energy using only HF:

$$\frac{1}{r_{12}} = \underbrace{\frac{1-\mathrm{erf}\left(\omega r_{12}\right)}{r_{12}}}_{\substack{\text{short-range}\\ \text{GGAs \& HF}}} + \underbrace{\frac{\mathrm{erf}\left(\omega r_{12}\right)}{r_{12}}}_{\substack{\text{long-range}\\ \text{HF only}}}$$



The exchange energy of the system is thus given by

$$E_{\text{exchange}}^{\text{LRC}} = \left(1 - C_{\text{HF}}\right) E_{\text{GGA exchange}}^{\text{short-range}} + C_{\text{HF}} E_{\text{HF exchange}}^{\text{short-range}} + E_{\text{HF exchange}}^{\text{long-range}}$$

where the exchange energies are evaluated using the components of $1/r_{12}$ above.

We optimized 2 parameters:

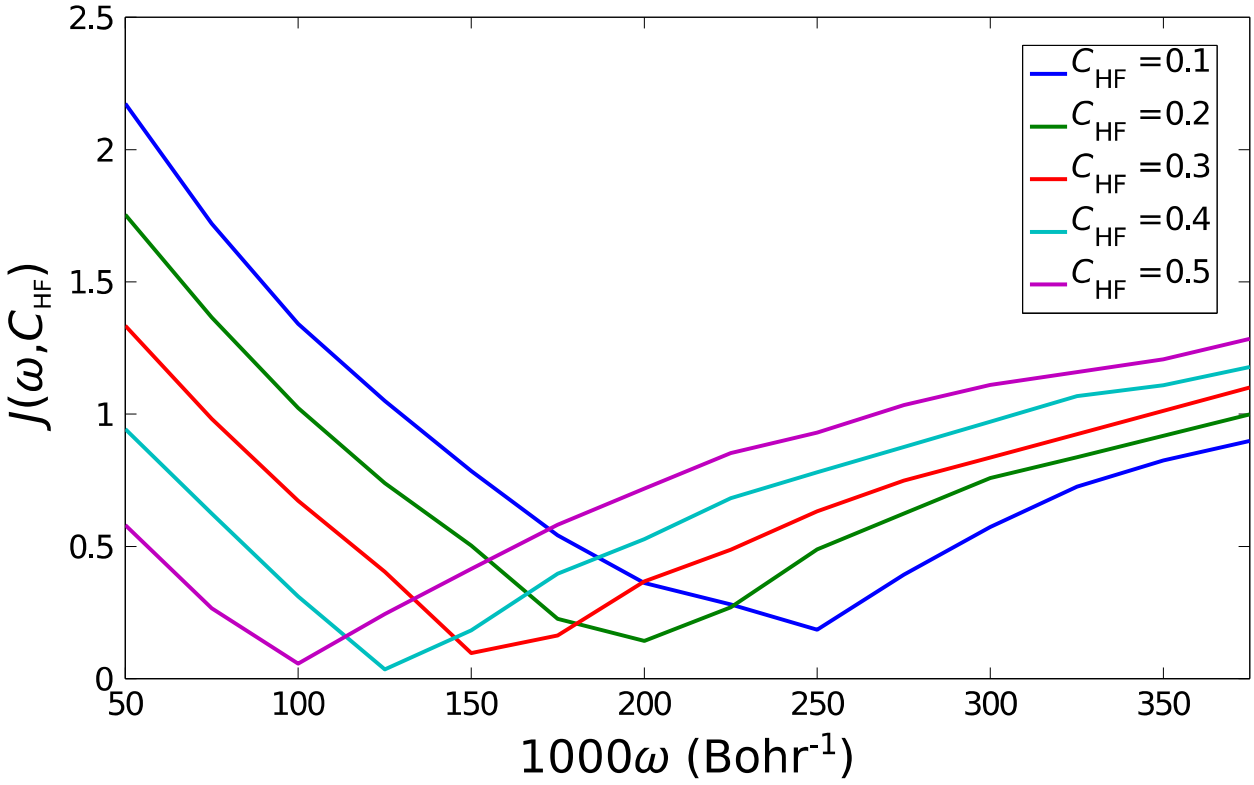
- ω—controls where the transition from a hybrid functional (GGAs and HF) to pure HF exchange takes place
- C_{HF}—controls the amount of HF exchange included at short-range

Our objective function to minimize J is based on matching Koopman's Theorem for the neutral and anion species and is given by

$$J\left(\omega, C_{\mathrm{HF}}\right) = \left|\varepsilon_{\mathrm{HOMO}}^{\omega, C_{\mathrm{HF}}}\left(\text{neutral}\right) - \mathrm{IP}\left(\text{neutral}\right)\right| + \left|\varepsilon_{\mathrm{HOMO}}^{\omega, C_{\mathrm{HF}}}\left(\text{anion}\right) - \mathrm{IP}\left(\text{anion}\right)\right|$$

where $\varepsilon_{\mathrm{HOMO}}^{\omega, C_{\mathrm{HF}}}$ is the homo energy and IP is the ionization potential.

To find the optimal values of ω and C_{HF}, we performed a series of single-point energy calculations (see figure below) on the species of interest over a grid of values of ω and C_{HF}. We then choose the set of parameters $\left\{\omega, C_{\mathrm{HF}}\right\}_{\mathrm{best}}$ that yield the lowest value of *J*.



The calculations necessary to calculate *J* for a give set $\left\{\omega, C_{\mathrm{HF}}\right\}$ are

- Single-point energy calculation on **neutral species**
- Single-point energy calculation on **anion**
- Single-point energy calculation on **cation**

The values in the objective function *J* are then obtained as follows:

- $\varepsilon_{\mathrm{HOMO}}^{\omega, C_{\mathrm{HF}}}$ is the larger of the alpha and beta occupied molecular orbital energies
- $\mathrm{IP}\left(\text{neutral}\right) = E\left(\text{cation}\right) - E\left(\text{neutral}\right)$
- $\mathrm{IP}\left(\text{anion}\right) = E\left(\text{anion}\right) - E\left(\text{neutral}\right)$

Examples of input file templates necessary to tune a LRC hybrid functional follow.

Also included below is a sample input file for a CDFT-CI calculation, from which the CT state and its transition dipole moment are obtained.

Example Input File - Neutral Sample, Qchem format

```
$rem
EXCHANGE                gen
LRC_DFT                 true
OMEGA                   **n** [omega=n/1000 inverse bohr; suggested range: 50-375]
BASIS                   6-31G
MEM_TOTAL               8000
MEM_STATIC              2000
SYMMETRY                false
SYM_IGNORE              true
INCDFT                  false
MAX_SCF_CYCLES          150
UNRESTRICTED            true
$end

$xc_functional
      C     PBE       1.00
      X     wPBE      **(1-C_HF)**
      X     HF        **C_HF**
$end

$molecule
0  1
C        -7.094846    0.501463   -0.983261
H        -7.683371    0.918014   -1.798475
C        -5.701571    0.528436   -1.046879
H        -5.190406    0.963806   -1.898302
C        -4.988684   -0.009588    0.020957
C        -5.685285   -0.551322    1.097716
H        -5.161040   -0.983570    1.942820
```

C	-7.079314	-0.531592	1.051985
H	-7.655256	-0.951177	1.874610
C	-2.895889	1.250407	0.069619
C	-1.409281	1.229090	0.069133
C	-0.712306	-0.001300	0.003223
C	-1.405263	-1.234121	-0.060007
C	-2.891734	-1.260672	-0.053439
C	-0.700987	-2.426083	-0.127406
H	-1.255600	-3.357010	-0.177364
C	0.706205	-2.423641	-0.129725
H	1.263905	-3.352633	-0.181286
C	1.406491	-1.229162	-0.065047
C	0.709403	0.001148	0.000449
C	1.402474	1.233875	0.063547
C	0.698292	2.425905	0.130909
H	1.252958	3.356806	0.180691
C	-0.708896	2.423507	0.133584
H	-1.266545	3.352517	0.185410
C	2.888959	1.260494	0.057037
C	2.893126	-1.250617	-0.064115
C	4.986170	0.008744	-0.007236
C	5.694055	-0.545855	1.055574
H	5.178939	-0.993889	1.897964
C	7.087563	-0.518832	0.998690
H	7.672040	-0.948242	1.810148
C	7.081829	0.544672	-1.020793
H	7.661676	0.976357	-1.834365
C	5.688060	0.566161	-1.072591
H	5.168121	1.012245	-1.913060
N	-7.785660	-0.016829	0.038808

N -3.543261 -0.006378 0.013004

N 3.540908 0.006073 -0.005046

N 7.783385 0.014238 -0.012337

O -3.535186 2.285820 0.119891

O -3.527876 -2.297904 -0.104842

O 3.524618 2.297965 0.109799

O 3.532126 -2.286173 -0.114100

$end

Example Input File – Cation Sample, Qchem format

```
$rem
EXCHANGE                gen
LRC_DFT                 true
OMEGA                   **n** [omega=n/1000 inverse bohr; suggested range: 50-375]
BASIS                   6-31G
MEM_TOTAL               8000
MEM_STATIC              2000
SYMMETRY                false
SYM_IGNORE              true
INCDFT                  false
MAX_SCF_CYCLES          150
UNRESTRICTED            true
$end

$xc_functional
      C     PBE       1.00
      X     wPBE      **(1-C_HF)**
      X     HF        **C_HF**
$end

$molecule
1 2
C       -7.094846   0.501463   -0.983261
H       -7.683371   0.918014   -1.798475
C       -5.701571   0.528436   -1.046879
H       -5.190406   0.963806   -1.898302
C       -4.988684  -0.009588    0.020957
C       -5.685285  -0.551322    1.097716
H       -5.161040  -0.983570    1.942820
```

C	-7.079314	-0.531592	1.051985
H	-7.655256	-0.951177	1.874610
C	-2.895889	1.250407	0.069619
C	-1.409281	1.229090	0.069133
C	-0.712306	-0.001300	0.003223
C	-1.405263	-1.234121	-0.060007
C	-2.891734	-1.260672	-0.053439
C	-0.700987	-2.426083	-0.127406
H	-1.255600	-3.357010	-0.177364
C	0.706205	-2.423641	-0.129725
H	1.263905	-3.352633	-0.181286
C	1.406491	-1.229162	-0.065047
C	0.709403	0.001148	0.000449
C	1.402474	1.233875	0.063547
C	0.698292	2.425905	0.130909
H	1.252958	3.356806	0.180691
C	-0.708896	2.423507	0.133584
H	-1.266545	3.352517	0.185410
C	2.888959	1.260494	0.057037
C	2.893126	-1.250617	-0.064115
C	4.986170	0.008744	-0.007236
C	5.694055	-0.545855	1.055574
H	5.178939	-0.993889	1.897964
C	7.087563	-0.518832	0.998690
H	7.672040	-0.948242	1.810148
C	7.081829	0.544672	-1.020793
H	7.661676	0.976357	-1.834365
C	5.688060	0.566161	-1.072591
H	5.168121	1.012245	-1.913060
N	-7.785660	-0.016829	0.038808

N -3.543261 -0.006378 0.013004

N 3.540908 0.006073 -0.005046

N 7.783385 0.014238 -0.012337

O -3.535186 2.285820 0.119891

O -3.527876 -2.297904 -0.104842

O 3.524618 2.297965 0.109799

O 3.532126 -2.286173 -0.114100

$end

Example Input File – Anion Sample, Qchem format

```
$rem
EXCHANGE                gen
LRC_DFT                 true
OMEGA                   **n** [omega=n/1000 inverse bohr; suggested range: 50-375]
BASIS                   6-31G
MEM_TOTAL               8000
MEM_STATIC              2000
SYMMETRY                false
SYM_IGNORE              true
INCDFT                  false
MAX_SCF_CYCLES          150
UNRESTRICTED            true
$end

$xc_functional
      C     PBE       1.00
      X     wPBE      **(1-C_HF)**
      X     HF        **C_HF**
$end

$molecule
-1 2
C       -7.094846   0.501463   -0.983261
H       -7.683371   0.918014   -1.798475
C       -5.701571   0.528436   -1.046879
H       -5.190406   0.963806   -1.898302
C       -4.988684  -0.009588    0.020957
C       -5.685285  -0.551322    1.097716
H       -5.161040  -0.983570    1.942820
```

C	-7.079314	-0.531592	1.051985
H	-7.655256	-0.951177	1.874610
C	-2.895889	1.250407	0.069619
C	-1.409281	1.229090	0.069133
C	-0.712306	-0.001300	0.003223
C	-1.405263	-1.234121	-0.060007
C	-2.891734	-1.260672	-0.053439
C	-0.700987	-2.426083	-0.127406
H	-1.255600	-3.357010	-0.177364
C	0.706205	-2.423641	-0.129725
H	1.263905	-3.352633	-0.181286
C	1.406491	-1.229162	-0.065047
C	0.709403	0.001148	0.000449
C	1.402474	1.233875	0.063547
C	0.698292	2.425905	0.130909
H	1.252958	3.356806	0.180691
C	-0.708896	2.423507	0.133584
H	-1.266545	3.352517	0.185410
C	2.888959	1.260494	0.057037
C	2.893126	-1.250617	-0.064115
C	4.986170	0.008744	-0.007236
C	5.694055	-0.545855	1.055574
H	5.178939	-0.993889	1.897964
C	7.087563	-0.518832	0.998690
H	7.672040	-0.948242	1.810148
C	7.081829	0.544672	-1.020793
H	7.661676	0.976357	-1.834365
C	5.688060	0.566161	-1.072591
H	5.168121	1.012245	-1.913060
N	-7.785660	-0.016829	0.038808

N -3.543261 -0.006378 0.013004

N 3.540908 0.006073 -0.005046

N 7.783385 0.014238 -0.012337

O -3.535186 2.285820 0.119891

O -3.527876 -2.297904 -0.104842

O 3.524618 2.297965 0.109799

O 3.532126 -2.286173 -0.114100

$end

Example Input File – CDFT-CI calculation, Qchem format

```
$rem
jobtype                     sp
basis                       cc-PVDZ
exchange                    gen
lrc_dft                     true
omega                       125
symmetry                    off
mem_total                   8000
mem_static                  2000
unrestricted                true
cdftci                      true
cdftci_skip_promolecules    true
cdftci_print                1
$end

$xc_functional
      C     PBE       1.00
      X     wPBE      **(1-C_HF)**
      X     HF        **C_HF**
$end

$cdft
1.0
1.0 1  44
1.0
1.0 1  44  s
----------
0.0
0.0  1  44
```

0.0

0.0 1 44 s

$end

$molecule

0 1

C	-7.094846	0.501463	-0.983261
H	-7.683371	0.918014	-1.798475
C	-5.701571	0.528436	-1.046879
H	-5.190406	0.963806	-1.898302
C	-4.988684	-0.009588	0.020957
C	-5.685285	-0.551322	1.097716
H	-5.161040	-0.983570	1.942820
C	-7.079314	-0.531592	1.051985
H	-7.655256	-0.951177	1.874610
C	-2.895889	1.250407	0.069619
C	-1.409281	1.229090	0.069133
C	-0.712306	-0.001300	0.003223
C	-1.405263	-1.234121	-0.060007
C	-2.891734	-1.260672	-0.053439
C	-0.700987	-2.426083	-0.127406
H	-1.255600	-3.357010	-0.177364
C	0.706205	-2.423641	-0.129725
H	1.263905	-3.352633	-0.181286
C	1.406491	-1.229162	-0.065047
C	0.709403	0.001148	0.000449
C	1.402474	1.233875	0.063547
C	0.698292	2.425905	0.130909
H	1.252958	3.356806	0.180691
C	-0.708896	2.423507	0.133584

H	-1.266545	3.352517	0.185410
C	2.888959	1.260494	0.057037
C	2.893126	-1.250617	-0.064115
C	4.986170	0.008744	-0.007236
C	5.694055	-0.545855	1.055574
H	5.178939	-0.993889	1.897964
C	7.087563	-0.518832	0.998690
H	7.672040	-0.948242	1.810148
C	7.081829	0.544672	-1.020793
H	7.661676	0.976357	-1.834365
C	5.688060	0.566161	-1.072591
H	5.168121	1.012245	-1.913060
N	-7.785660	-0.016829	0.038808
N	-3.543261	-0.006378	0.013004
N	3.540908	0.006073	-0.005046
N	7.783385	0.014238	-0.012337
O	-3.535186	2.285820	0.119891
O	-3.527876	-2.297904	-0.104842
O	3.524618	2.297965	0.109799
O	3.532126	-2.286173	-0.114100

$end

References

(1) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 3540–3544.