Supplementary Material (ESI) for Journal of Materials Chemistry


# Supplementary materials

## Interactions between Tripodal Porphyrin Hosts and Single Walled Carbon Nanotubes: an Experimental and Theoretical (DFT) Account

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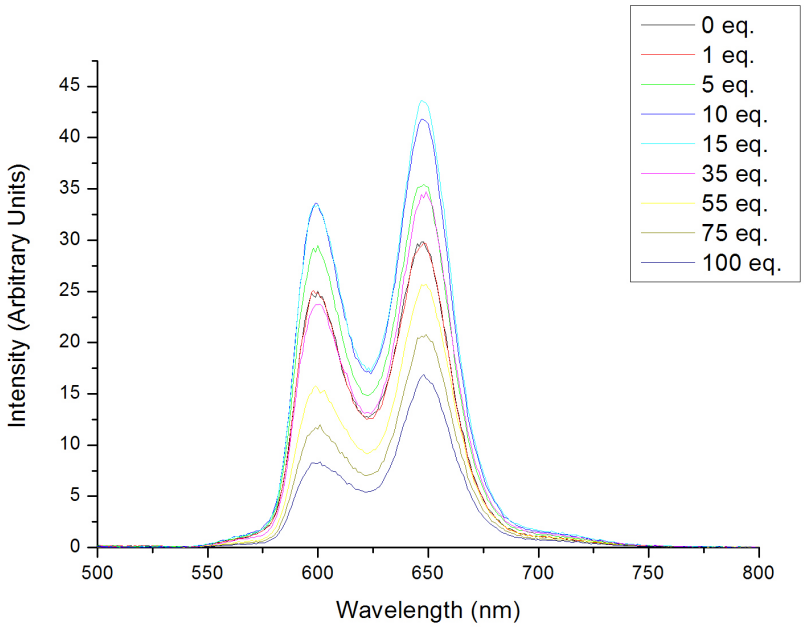
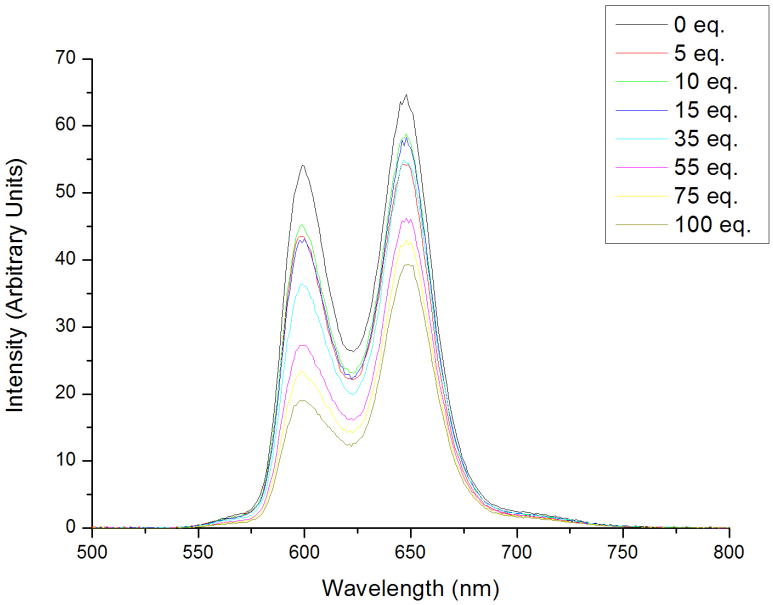
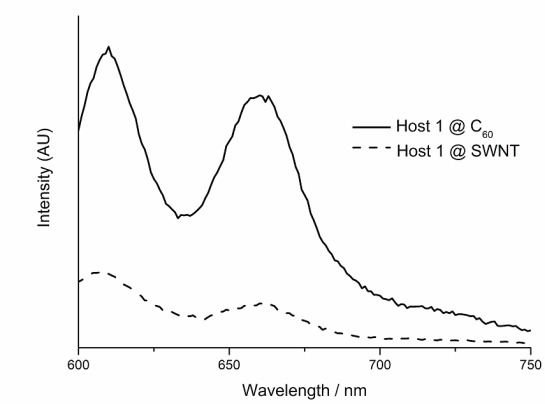
**Fluorescence quenching of free porphyrin hosts 1 (top) and 2 (bottom) upon addition of excess $C_{60}$ ($\lambda_{ex}$=420 nm, 7.5 µM in toluene).**



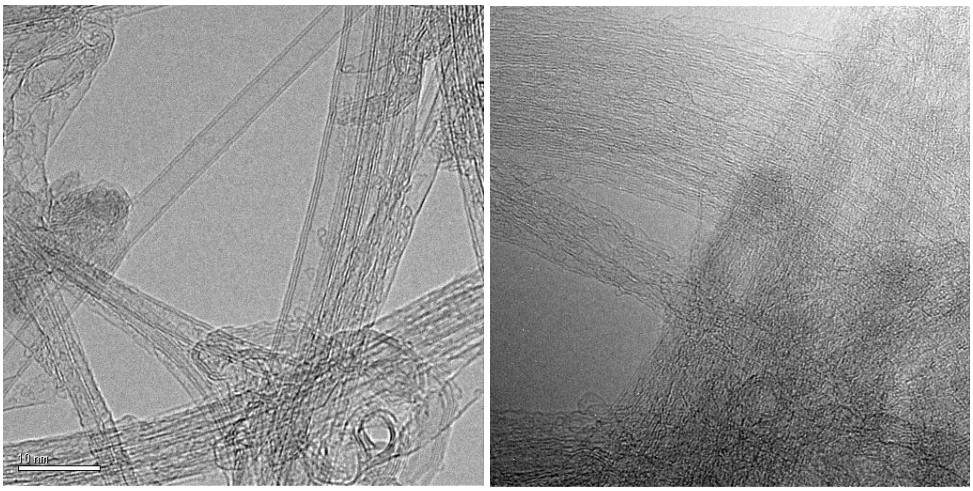
## Fluorescence spectra ($\lambda_{ex}$=500 nm) of the $C_{60}$: prophyrin 1 complex 4:2.

Single crystals of the complex were dissolved in pure DMF to give 0.15 mM solutions. For SWNT@host 1 composite 0.2 mg / mL dispersions of composite in DMF were prepared.

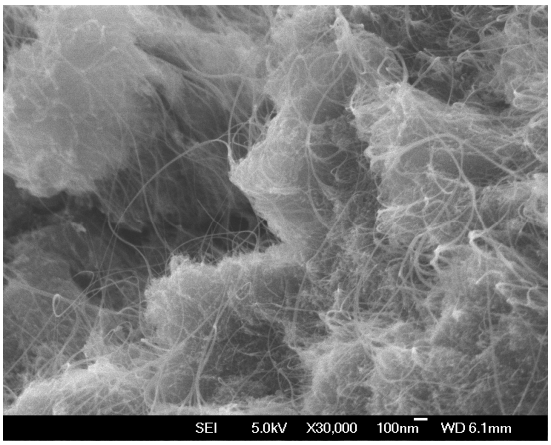



## HR TEM of the purified SWNTs

CVD-made, SWAN quality SWNTs were deposited on copper grid from a EtOH dispersion prior to treatment with porphyrin hosts. The images show that (although agglomerated in large bundles following purification) the nanotube walls are remarkably clean (Scalebar 10 nm used throughout).

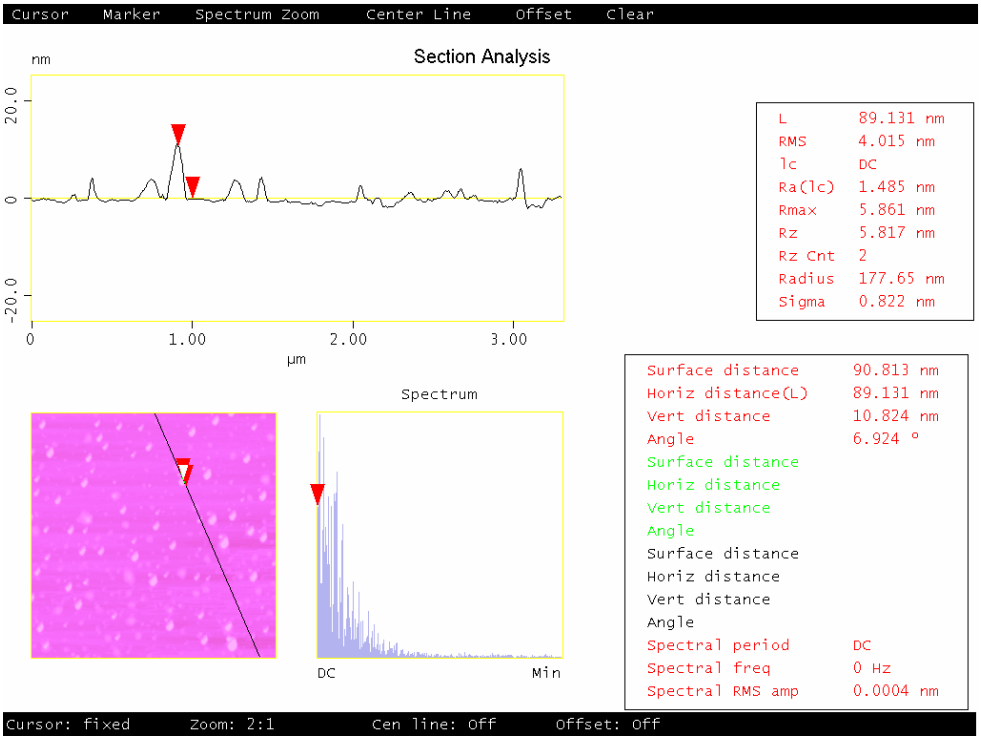


## SEM micrograph of purified SWNT prior to the treatment with porphyrin hosts.

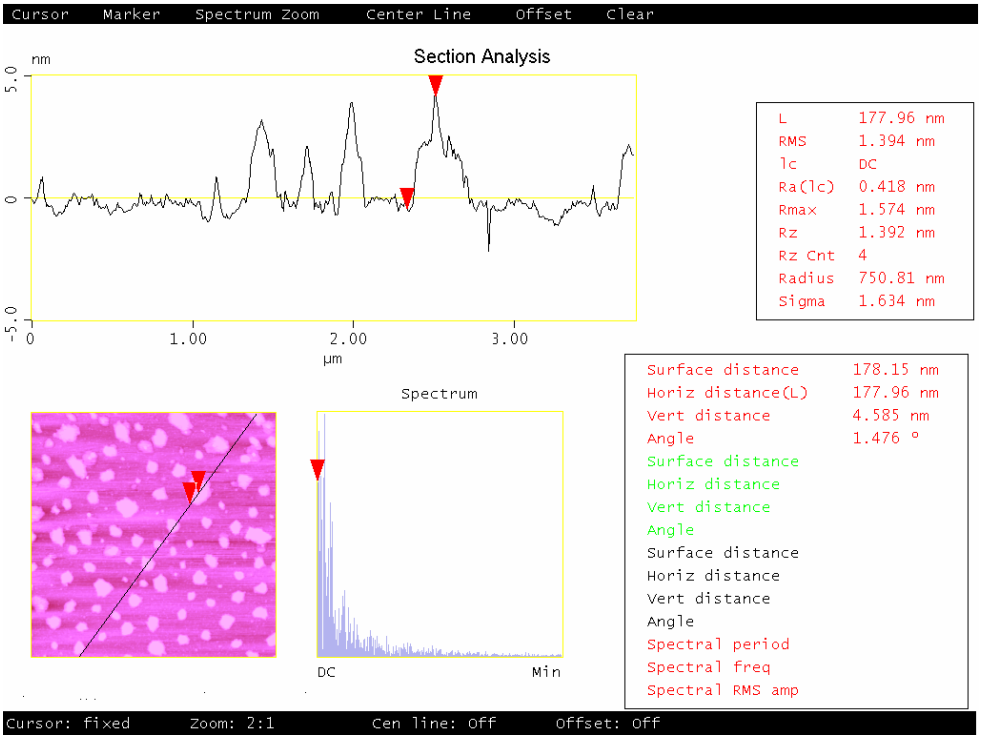


## TM AFM data analysis:

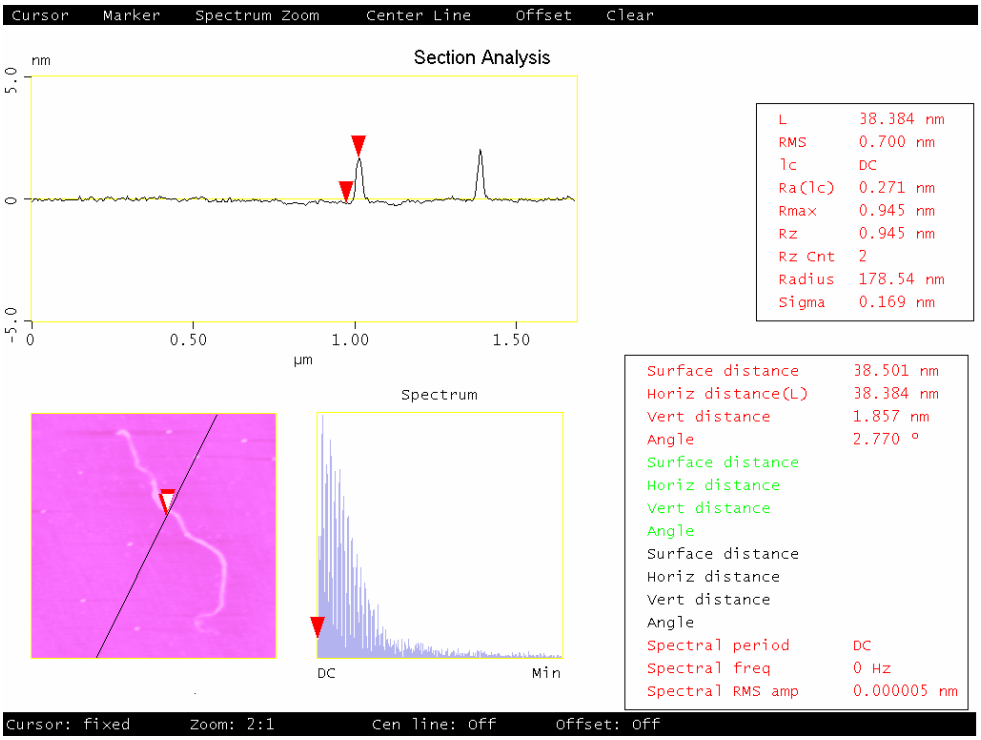
i) Porphyrin host **1** on mica, spin coated from DMF solutions (0.156 mM).



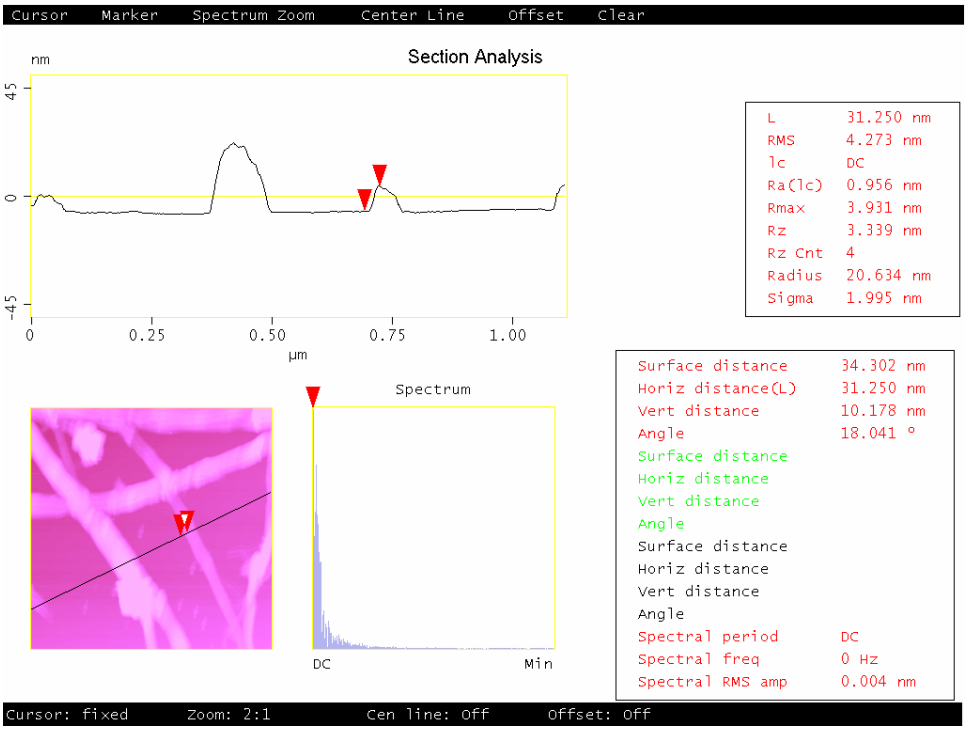

ii) Porphyrin host **2** on mica, spin coated from DMF solutions (0.156 mM).



iii) Porphyrin host **1** on SWNTs, spin coated on mica from DMF dispersions (0.2 mg / mL).

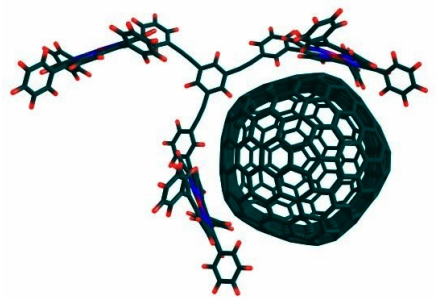



iv) Porphyrin host **2** on SWNTs, spin coated on mica from DMF dispersions (0.2 mg / mL).



## DFT Calculations – data analysis

***Complex between a simplified porphyrin host (ZnP) and a [10,10] Nanotube***



**Optimised structure of SWNT@porphyrin host**

No of atoms in the porphyrin unit = 243
No of atoms in the nanotube (10, 10) = 400

$E_{Porphyrin\_SWNT}$ = -94092.103046 eV

$E_{Porphyringhost\_SWNT}$ = -62132.664612 eV

$E_{Porphyrin\_SWNTghost}$ = -31957.392390 eV

$E_{bind} = E_{Porphyrin\_SWNT} - (E_{Porphyringhost\_SWNT} + E_{Porphyrin\_SWNTghost})$

= -94092.103046 – (-62132.664612 + -31957.392390) eV

= **- 2.0460 eV (-197.41255 kJ/mol, -47.183820684 kcal/mol)**

**Structural Parameters (calculated)**

| **Zn-N (Å)** | **N-Zn-N (Angle)** |
|---|---|
| 2.01 | 179.4, 176.2 |
| 2.03 | 90.0, 90.6 |
| 2.04 | 89.5, 89.7 |
| | |
| 2.02 | 175.7, 178.3 |
| 2.03 | 90.1, 91.0 |
| 2.04 | 89.2, 89.6 |
| 2.05 | |

**Porphyrin unit not interacting with nanotube**

2.03 179.8, 177.3

2.04 90.0, 90.0

89.8, 90.1

**C-H distances** 1.09, 1.10 Å

**Zn-C distances**

3.30, 3.32 Å 3.47, 3.59 Å

3.34, 3.30 Å

**C-C distance (shortest) between $C_{60}$ and porphyrin plane**

3.33 Å 3.36 Å

3.48 Å 3.54 Å

## Charge Analysis in composites

### Nanotube

Carbons

| Total valence electrons | Total valence electrons in composite | Charge gain by Nanotube |
|---|---|---|
| 400 x 4 = 1600 | 1600.003 | **0.003 (0.0000075/C)** |

### Porphyrin

Nitrogen

| Total valence electrons | Total valence electrons in composite | Charge gain by Nitrogens |
|---|---|---|
| 12 x 5 = 60 | 63.689 | **3.689(0.3074/N)** |

Zinc

| Total valence electrons | Total valence electrons in composite | Charge lost by Zincs |
|---|---|---|
| 3 x 12 = 36 | 33.474 | **2.526 (0.84/Zn)** |

Hydrogen

| Total valence electrons | Total valence electrons in composite | Charge lost by Hydrogen |
|---|---|---|
| 84 x 1 = 84 | 72.338 | **11.662 (0.139/H)** |

Carbons

| Total valence electrons | Total valence electrons in composite | Charge gain by Carbons |
|---|---|---|
| 144 x 4 = 576 | 586.489 | **10.49 (0.0729/C)** |

| | **Gain** | | **Lost** |
|---|---|---|---|
| **Nanotube** | | | |
| Carbons | 0.003 | | |
| **Porphyrin** | | | |
| | | Zinc | 2.526 |
| Nitrogens | 3.689 | | |
| Carbons | 10.490 | Hydrogens | 11.662 |
| | ---------- | | ---------- |
| | **14.182** | | **14.208** |

**Charge Analysis In Nano$_{ghost}$ _Porphyrins**

**Nanotube**

Carbon

| Total valence electrons | Total valence electrons in composite | Charges on Nanotube |
|---|---|---|
| ---------- | ---------- | **-0.005 (0.0000125/C)** |

**Porphyrins**

Nitrogen

| Total valence electrons | Total valence electrons in composite | Charge gain by Nitrogens |
|---|---|---|
| 12 x 5 = 60 | 63.777 | **3.777(0.31475/N)** |

Zinc

| Total valence electrons | Total valence electrons in composite | Charge lost by Zincs |
|---|---|---|
| 3x 12 = 36 | 33.359 | **2.641(0.88/Zn)** |

Carbon

| Total valence electrons | Total valence electrons in composite | Charge gain by Carbons |
|---|---|---|
| 144 x 4 = 576 | 586.677 | **10.677 (0.074/C)** |

Hydrogen

| Total valence electrons | Total valence electrons in composite | Charge lost by Hydrogen |
|---|---|---|
| 84 x 1 = 84 | 72.171 | **11.829 (0.141/H)** |

**Charge Analysis In Nano_Porphyrin$_{ghost}$**

**Nanotube**

Carbon

| Total valence electrons | Total valence electrons in composite | Charges gain by $C_{60}$ |
|---|---|---|
| 400x4 =1600 | 1600.109 | **0.109 (0.00027/C)** |

**Porphyrins**

Nitrogen

| Total valence electrons | Total valence electrons in composite | Charges on Nitrogens |
|---|---|---|
| ---------- | ---------- | **0.009 (0.00075/N)** |

Zinc

| Total valence electrons | Total valence electrons in composite | Charge lost by Zincs |
|---|---|---|
| ---------- | ---------- | **-0.079 (0.0263/Zn)** |

Carbon

| Total valence electrons | Total valence electrons in composite | Charges on Carbons |
|---|---|---|
| ---------- | ---------- | **0.001 (0.000001/C)** |

Hydrogen

| Total valence electrons | Total valence electrons in composite | Charges on Hydrogen |
|---|---|---|
| ---------- | ---------- | **-0.034 (0.0004/H)** |

**CHARGE TRANSFER ANALYSIS**

**Nanotube**

| Composites | NANO$_{ghost}$_Porphyrins | NANO_Porphyrins$_{ghost}$ |
|---|---|---|
| **0.003** | **-0.005** | **0.109** |

## BSSE equation

$E_{bind} = E_{Comp} - [E_{Nanoghost\_Porphyrins} + E_{Nano\_Porphyringhost}]$

$CT = Charge_{gain/lost}(composites) - [Charge_{gain/lost}(Nanoghost\_Porphyrins) + Charge_{gain/lost}(Nano\_Porphyringhost)]$

$CT = \mathbf{0.003} - [\mathbf{-0.005} + \mathbf{0.109}]$

$CT = \mathbf{-0.101\ e}$

## Charge transfer is from Nanotube to Porphyrins [0.101e]

## Geometry optimisations:

**$C_{60}$ complex (4 $C_{60}$: 2 porphyrin host) using the simplified tripodal porphyrin trimer (ZnP)**

$E_{TetraC60\_Tripor}$ = -101133.08 eV
$E_{TetraC60}$ = -37211.92 eV
$E_{Tripodaltrimer}$ = -63914.28 eV
$E_{TetraC60ghost\_Porphyrin}$ = -63915.45 eV
$E_{TetraC60\_Porphyringhost}$ = -37212.77 eV

$E_{bind} = E_{TetraC60\_Tripor} - (E_{TetraC60} + E_{Tripodaltrimer})$
= -101133.08 – (-63914.28 + -37211.92) eV
= **-6.88 eV [663.82 kJ/mol, 158.6528 kcal/mol] or 1.72 eV/$C_{60}$**
= **-0.0286 eV/C [-2.76 kJ/mol, -0.66 kcal/mol]**

$E_{bind} = E_{TetraC60\_Tripor} - (E_{TetraC60ghost\_Porphyrin} + E_{TetraC60\_Porphyringhost})$
= -101133.08 – (-63914.28 + -37212.77) eV
= **-4.860 eV [-468.92 kJ/mol, 112.08 kcal/mol] or -1.215 eV/$C_{60}$**
= **-0.02 eV/C [-1.93 kJ/mol, -0.46 kcal/mol]**

**SWNT complex with the simplified tripodal porphyrin trimer ZnP**

$E_{Porphyrin\_SWNT}$ = -94092.103046 eV
$E_{Porphyrin}$ = -31956.78 eV
$E_{SWNT}$ = -62132.37 eV
$E_{Porphyringhost\_SWNT}$ = -62132.664612 eV

$E_{Porphyrin\_SWNTghost}$ = -31957.392390 eV

$E_{bind}$ = $E_{Porphyrin\_SWNT}$ – ($E_{SWNT}$ + $E_{Porphyrin}$)

= -94092.103 – (-62132.37 + -31956.78 ) eV

= **-2.953 eV (-284.92 kJ/mol, -68.096 kcal/mol)**

= **- 0.0074 eV/C**

$E_{bind}$ = $E_{Porphyrin\_SWNT}$ – ($E_{Porphyringhost\_SWNT}$ + $E_{Porphyrin\_SWNTghost}$)

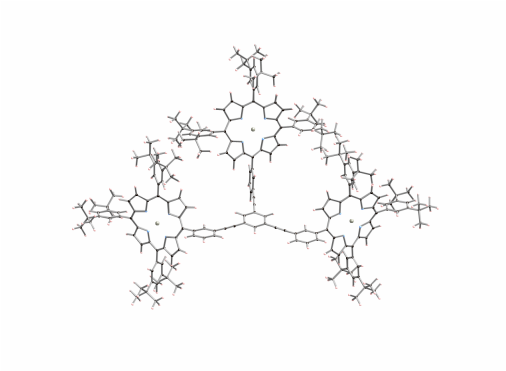
= - 94092.103046 – (-62132.664612 + -31957.392390) eV

= **- 2.0460 eV (-197.41255 kJ/mol, -47.183820684 kcal/mol)**

= **- 0.0051eV/C**

| | **Uncorrected** | | | **Corrected** | | |
|---|---|---|---|---|---|---|
| **Type** | **$E_b$(unc)** | **$E_b$(unc)/$C_{60}$ or SWNT** | **$E_b$(unc)/C** | **$E_b$(CP)** | **$E_b$(CP)/$C_{60}$ or SWNT** | **$E_b$(CP)/C** |
| $C_{60}$_Porphyrin complex (4 $C_{60}$:2 hosts) | -6.88 | -1.72 | -0.0286 | -4.86 | -1.215 | -0.02 |
| SWNT_Porphyrin composite | -2.953 | -2.953 | -0.0074 | -2.046 | -2.046 | -0.005 |

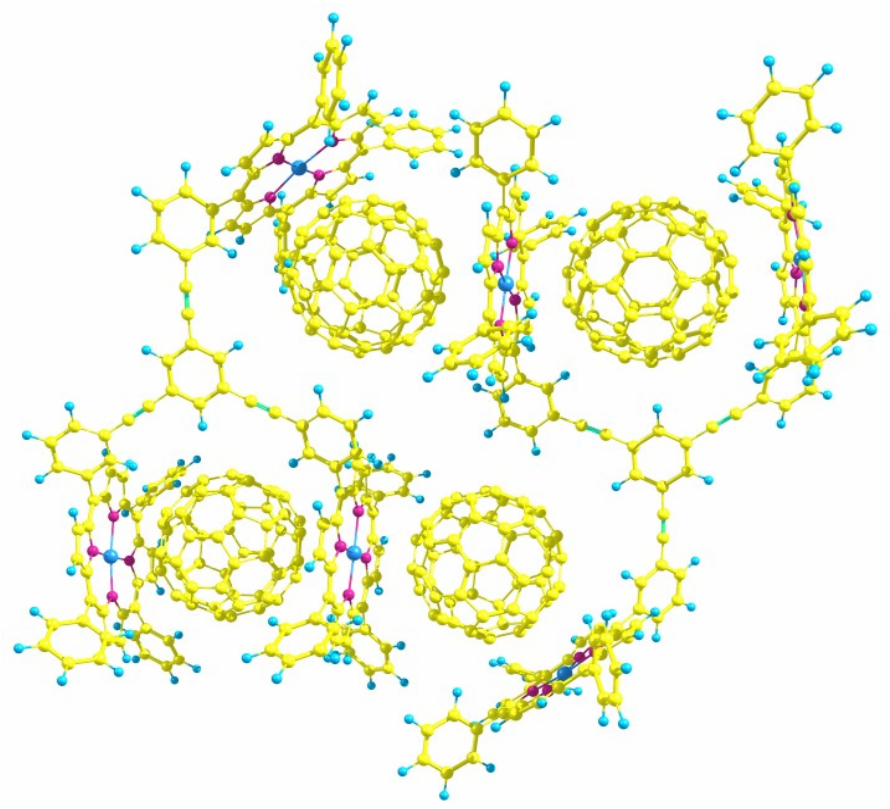
## *SCF energies for three different host geometries*



**Tripodal trimer**

| **Structure** | **SCF energy** |
|---|---|
| Propeller-type | -31957.33 eV |
| Bowl-type | -31957.17 eV |
| Structure resembling crystal structure of **1** (shown above) | -31957.26 eV |

## *SCF energies for a simplified $C_{60}$:porphyrin host 4:2 complex*



**Tetra $C_{60}$: Porphyrin complex**

$E_{TetraC60\_Tripor}$ = -101133.08 eV.

$TetraC_{60ghost}$_Porphyrin = -63915.45 eV.

$TetraC_{60}$_Porphyrin = -37212.77 eV.

$E_{bind}$ = $E_{TetraC60\_Tripor}$ – ($TetraC_{60ghost}$_Porphyrin + $TetraC_{60}$_Porphyrin)

= -101133.08 – (-63915.45 + -37212.77) eV

= **-4.860 eV [-468.92 kJ/mol, 112.08 kcal/mol] or -1.215 eV/$C_{60}$**

= **-0.02 eV/C [-1.93 kJ/mol, -0.46 kcal/mol]**

**Optimised structure of $TetraC_{60}$_Porphyrin**

**Calculated Structural Parameters**

| **Distance Zn-N (Å)** | **Angles N-Zn-N (°)** |
|---|---|
| 2.04 | 178.7, 177.4 |
| 2.03 | 90.4, 90.1 |
| | 89.6, 89.8 |

| | |
|---|---|
| 2.03 | 174.1, 174.4 |
| 2.04 | 90.7, 90.0 |
| 2.05 | 89.6, 89.1 |
| | |
| 2.01 | 173.0, 178.0 |
| 2.03 | 91.5, 90.4 |
| 2.05 | 89.2, 88.7 |
| 2.03 | 179.0, 174.0 |
| 2.04 | 90.0, 90.1 |
| | 89.8, 89.8 |
| | |
| 2.02 | 178.2, 178.3 |
| 2.03 | 90.5, 90.5 |
| 2.04 | 89.4, 89.5 |
| | |
| 2.02 | 176.7, 173.6 |
| 2.03 | 90.6, 90.3 |
| 2.04 | 89.8, 88.8 |
| 2.05 | |

**C-C Distances in $C_{60}$**

| Type | (6,6) | (6,5) |
|---|---|---|
| $C_{60}$ (inside the porphyrin complex) | 1.390, 1.395, 1.396 Å | 1.440 , 1.446 Å |
| $C_{60}$ (outside the porphyrin complex) | 1.393 Å | 1.441 Å |

**Zn-C distances**

| | | |
|---|---|---|
| 2.83, 2.93 Å | 2.90, 3.16 Å | 2.81, 2.95 Å |
| 3.08, 3.02 Å | 2.94, 3.14 Å | 2.79, 3.13 Å |
| 3.03, 2.85 Å | 2.97, 3.06 Å | |

**Shortest C-C distance between $C_{60}$ and porphyrin plane**

| | |
|---|---|
| 3.43 Å | 3.62 Å |
| 3.44 Å | 3.71 Å |

3.45 Å 3.73 Å

3.51 Å 3.77 Å

**Experimental values from X-ray diffraction structure of 1:C60 2:4 complex:**

**Zn-N (Å)**

Zn1 . N1 . 2.047(17)
Zn1 . N2 . 2.04(2)
Zn1 . N3 . 2.035(18)
Zn1 . N4 . 2.057(17)

Zn2 . N5 . 2.007(18)
Zn2 . N6 . 2.024(17)
Zn2 . N7 . 2.012(19)
Zn2 . N8 . 2.015(17)

Zn3 . N9 . 2.053(18)
Zn3 . N10 . 2.01(2)
Zn3 . N11 . 2.076(18)
Zn3 . N12 . 2.07(2)

Zn4 . N13 . 2.037(18)
Zn4 . N14 . 1.996(19)
Zn4 . N15 . 2.01(2)
Zn4 . N16 . 2.059(18)

Zn5 . N17 . 2.02(2)
Zn5 . N18 . 2.039(16)
Zn5 . N19 . 2.01(2)
Zn5 . N20 . 2.028(17)

Zn6 . N21 . 2.093(19)
Zn6 . N22 . 2.03(2)
Zn6 . N23 . 2.104(19)
Zn6 . N24 . 2.097(19)

**N-Zn-N (Angle)**

N1 . Zn1 . N2 . 90.0(7)
N1 . Zn1 . N3 . 173.9(8)
N2 . Zn1 . N3 . 90.2(7)
N1 . Zn1 . N4 . 90.0(7)
N2 . Zn1 . N4 . 173.0(8)
N3 . Zn1 . N4 . 89.0(7)

N5 . Zn2 . N6 . 90.7(8)
N5 . Zn2 . N7 . 178.4(7)
N6 . Zn2 . N7 . 90.2(8)
N5 . Zn2 . N8 . 88.4(7)

N6 . Zn2 . N8 . 177.0(8)
N7 . Zn2 . N8 . 90.7(7)

N9 . Zn3 . N10 . 91.1(7)
N9 . Zn3 . N11 . 167.9(8)
N10 . Zn3 . N11 . 89.6(7)
N9 . Zn3 . N12 . 88.1(7)
N10 . Zn3 . N12 . 168.2(8)
N11 . Zn3 . N12 . 88.7(7)

N13 . Zn4 . N14 . 89.9(7)
N13 . Zn4 . N15 . 173.7(9)
N14 . Zn4 . N15 . 90.1(8)
N13 . Zn4 . N16 . 88.9(7)
N14 . Zn4 . N16 . 175.8(8)
N15 . Zn4 . N16 . 90.6(8)

N17 . Zn5 . N18 . 90.8(8)
N17 . Zn5 . N19 . 177.8(7)
N18 . Zn5 . N19 . 91.0(8)
N17 . Zn5 . N20 . 89.7(8)
N18 . Zn5 . N20 . 174.8(7)
N19 . Zn5 . N20 . 88.4(8)

N21 . Zn6 . N22 . 87.3(7)
N21 . Zn6 . N23 . 169.2(8)
N22 . Zn6 . N23 . 89.5(8)
N21 . Zn6 . N24 . 91.0(7)
N22 . Zn6 . N24 . 168.9(8)
N23 . Zn6 . N24 . 90.2(7)

**$C_{60}$ radii: 3.539 ($C_{60}$(1)), 3.540 ($C_{60}$(3)) 3.546 ($C_{60}$(2)), 3.541 ($C_{60}$(4))**

**Other relevant parameters:**

| Zn porphyrin centre | Distance of $C_{60}$ centre to porphyrin best plane (Å) | Distance of $C_{60}$ surface to porphyrin best plane (Å) |
|---|---|---|
| Zn(1) | 6.211 ($C_{60}$(4)) | 2.670 |
| Zn(2) | 6.136 ($C_{60}$(1)), 6.462 ($C_{60}$(3)) | 2.597 ($C_{60}$(1)), 2.922 ($C_{60}$(3)) |
| Zn(3) | 6.112 ($C_{60}$(1)) | 2.573 |
| Zn(4) | 6.182 ($C_{60}$(4)) | 2.642 |
| Zn(5) | 6.094 ($C_{60}$(2)), 6.437 ($C_{60}$(4)) | 2.548 ($C_{60}$(2)), 2.896 ($C_{60}$(4)) |
| Zn(6) | 6.069 ($C_{60}$(2)) | 2.523 |

**Charge Analysis:**

***a) In porphyrin:C60 complex***

**C60:**

Carbons

| Total valence electrons | Total valence electrons in composite | Charge gain by $C_{60}$ |
|---|---|---|
| 240 x 4 = 960 | 960.032 | **0.032 (0.00013/C)** |

**Porphyrin:**

Nitrogen

| Total valence electrons | Total valence electrons in composite | Charge gain by Nitrogens |
|---|---|---|
| 24 x 5 = 120 | 126.664 | **6.664 (0.28/N)** |

Zinc

| Total valence electrons | Total valence electrons in composite | Charge lost by Zincs |
|---|---|---|
| 6 x 12 = 72 | 67.730 | **4.270 (0.71/Zn)** |

Hydrogen

| Total valence electrons | Total valence electrons in composite | Charge lost by Hydrogen |
|---|---|---|
| 168 x 1 = 168 | 144.668 | **23.332 (0.139/H)** |

Carbons

| Total valence electrons | Total valence electrons in composite | Charge gain by Carbons |
|---|---|---|
| 288 x 4 = 1152 | 1172.907 | **20.907 (0.07/C)** |

| | **Gain** | | **Lost** |
|---|---|---|---|
| **Bucky balls** | | | |
| Carbons | 0.032 | | |
| **Porphyrin** | | | |
| | | Zinc | 4.270 |
| Nitrogens | 6.664 | | |
| Carbons | 20.907 | Hydrogens | 23.332 |
| | --- | | --- |
| | **27.603** | | **27.602** |

### *b) In Buckyball$_{ghost}$ _Porphyrin*

**$C_{60}$**

Carbon

| Total valence electrons | Total valence electrons in composite | Charges on $C_{60}$ |
|---|---|---|
| ---------- | ---------- | **-0.088 (0.0015/C)** |

**Porphyrins**

Nitrogen

| Total valence electrons | Total valence electrons in composite | Charge gain by Nitrogens |
|---|---|---|
| 24 x 5 = 120 | 127.077 | **7.077 (0.295/N)** |

Zinc

| Total valence electrons | Total valence electrons in composite | Charge lost by Zincs |
|---|---|---|
| 6 x 12 = 72 | 67.161 | **4.839 (0.81/Zn)** |

Carbon

| Total valence electrons | Total valence electrons in composite | Charge gain by Carbons |
|---|---|---|
| 288 x 4 = 1152 | 1172.448 | **20.448 (0.071/C)** |

Hydrogen

| Total valence electrons | Total valence electrons in composite | Charge lost by Hydrogen |
|---|---|---|
| 168 x 1 = 168 | 144.390 | **23.610 (0.14/H)** |

### *c) In Buckyball_Porphyrin$_{ghost}$*

**C60**

Carbon

| Total valence electrons | Total valence electrons in composite | Charges gain by $C_{60}$ |
|---|---|---|
| 240x4 =960 | 960.226 | **0.2260 (0.001/C)** |

**Porphyrins**

Nitrogen

| Total valence electrons | Total valence electrons in composite | Charges on Nitrogens |
|---|---|---|
| ---------- | ---------- | **0.029 (0.0012/N)** |

Zinc

| Total valence electrons | Total valence electrons in composite | Charge lost by Zincs |
|---|---|---|
| ---------- | ---------- | **-0.341(0.057/Zn)** |

Carbon

| Total valence electrons | Total valence electrons in composite | Charges on Carbons |
|---|---|---|
| ---------- | ---------- | **0.0860 (0.0003/C)** |

Hydrogen

| Total valence electrons | Total valence electrons in composite | Charges on Hydrogen |
|---|---|---|
| ---------- | ---------- | **-0.001 (0.000006/H)** |

## CHARGE TRANSFER ANALYSIS:

**C60's**

| Composites | $Bucky_{ghost}$_Porphyrins | Bucky_$Porphyrins_{ghost}$ |
|---|---|---|
| **0.032** | **-0.088** | **0.226** |

**BSSE equation**

Ebind = EComp – [$E_{Buckyghost\_Porphyrins}$ + $E_{Bucky\_Porphyringhost}$]

CT = $Charge_{gain/lost}$ (composites) – [Charge $_{gain/lost}$ ($_{Buckyghost\_Porphyrins}$) + Charge $_{gain/lost}$ ($_{Bucky\_Porphyringhost}$)]

CT = **0.032** – [**-0.088** + **0.226**]

CT = **-0.106 e (0.00044/C) or 0.0265/$C_{60}$**

**Charge transfer from C60 to Porphyrins [0.106e//0.00044/C] or 0.0265/$C_{60}$**