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共軛有機聚合物的電子光譜電與光致電子轉移

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前 言

在過去十幾年來,有機共軛分子及高分子已成為新一代具有潛力的材料,已被應用在許多方向,例如發光二極體(light-emitting diodes(LEDs))¹⁻²,光放射電化學電池(light-emitting electrochemical cells)³,場效應電晶體(field-effect transistors)⁴⁻⁶,光二極體(photodiodes)⁷,太陽能電池(solar cells)⁸,固態雷射(solid-state lasers)⁹等。值得注意的是在發光二極體上的應用,現在,有機發光二極體已經達到可商業化的階段,低操作電壓,高壽命(lifetime>10000h),發光範圍涵蓋整個可見光區¹⁰,外部量子效率(external quantum efficiency)可高達9%¹¹。近年來,量子化學及固態物理方法提供許多單分子理論,經由大量的實驗資料,已經建立起單分子光電特性的輪廓,放光行為在無明顯的分子間作用時(稀溶液或惰性介質(inert matrix)),是從第一個激發態(excited state)至基態(ground state),服從 Kasha 規則¹²,實驗結果有時候可與單分子計算結果吻合,但若分子間作用力不可忽略時,將對電子與發光性質相對於單分子產生極大的變化¹³⁻¹⁶,因此,分子間的作用成為了解固態光物理行為的重要因素。

處理共軛分子的電子結構,最簡單的量子化學方法是利用單電子 Hückel 模型,但是這樣的處理方式無法明確的處理電子間交互作用效應 (electron-correlation effects)以及電子結構與分子幾何結構之間的影響,這樣的多體效應(many-body effects)對於處理分子激發態與分子間交互作用這兩種情況是非常明顯的。因此我們將使用半經驗量子化學方法 Pariser-Parr-Pople (PPP) 模型將分子結構訊息考慮進來並且將電子間排斥平均場利用自洽場 (self-consistent field)方法計算出來,這樣的考量可以將電子結構與幾何結構相互關係定量算出。而電子間的交互作用在處理激發態方面顯的格外重要,以單鍵及雙鍵交替且電子數為偶數的多稀(polyene)分子為例,由單電子模型(Hückel, PPP)方法處理可以獲得一組電子分子軌域,電子填入這些軌域可形成所謂的電子組態(electronic configuration),這樣建構出的波函數可用 Slater 行列式來表示,其最低能量的組態是所有考慮的電子填入較低能量的分子軌域,而構成所謂的單態基態(singlet ground state),其對稱性為 A_g ;而最低的單光子可躍 (one-photon allowed)激發態可表示為將一個電子由最高的填滿軌域(highest occupied molecular orbital(HOMO))提陞至最低的未填滿軌域(lowest unoccupied molecular orbital(LUMO)),其對稱性為 B_u ;其他對稱性為 A_g 的單光子不可躍(one-photon forbidden)激發態能量都比 $1B_u$ 激發態高,例如,將一個電子由 HOMO 提陞至 LUMO+1 或由 HOMO-1 提陞至 LUMO 或由 HOMO 提陞兩個電子到 LUMO 均需要較 $1B_u$ 態更多的能量。但是,如果將電子間的交互作用考

慮進來將產生不同的結果,考慮電子間的交互作用有許多方法,例如利用組態作用(configuration interaction(CI))方法,每一個電子態均為多個電子組態的線性組合而成,以多烯分子而言,單電子激發 HOMO 至 LUMO+1 以及 HOMO-1 至 LUMO 及雙電子激發 HOMO 至 LUMO 三個電子組態會產生非常強的作用造成 $2A_g$ 電子態較 $1B_u$ 電子態能量低,因此,多烯分子之基態與最低單態激發態互為不可躍狀態,由 Kasha 規則可知,多烯分子的放光效率非常低。在本篇論文我們也將考慮電子的交互作用,即利用上述的組態作用方法,而我們所取用的基底組(basis set)為所有單電子單態激發波函數,也就是說每一個激發態波函數為這些基底的線性組合而得,這樣的方法是所謂的單組態作用(single configuration interaction(SCI)),若選取的基底組為所有單激發組態,這樣的方法為符合尺度一致(size consistent),也就是說當比較不同長度的分子時,不因計算本身方法而導致嚴重的錯誤而且這個方法經常可以獲得非常接近實驗上所測得的激發態能量。另外必須注意的是,利用單組態作用的方法所計算出來的第一個激發態為 $1B_u$ 態非 $2A_g$ 態,這並不重要,因為我們關心的是可與基態互為可躍遷的激發態,進而探討分子間作用對此激發態造成的影響。

在處理分子間作用方面,常見的有兩種方法,激子模型(exciton model)與超分子近似(supermolecular approach)方法。將這兩種方法互相比較,超分子近似方法是比較準確的,因為此方法是將雙分子考慮成一個分子,所以其分子軌域會在整個大分子上產生非定域化(delocalized)分佈,這樣的方法會將定域激子(local

exciton)與電荷轉移激子(charge-transfer (CT) exciton)一起考慮進來;而激子模型只有考慮定域激子的貢獻。雖然超分子近似方法完整的考慮定域激子與電荷轉移激子這兩種貢獻,但是,這樣的計算方法卻不易將這兩種激子定量分開,除非可以正確取得激發態的波函數;因此,我們將利用變分方法(variation)明確定義所使用的基底組,包含這兩種激子,而其所有矩陣元(matrix element)均可利用單一分子所得到的結果來估計,此方法稱為 molecules in molecules(MIM)方法,僅利用基態波函數即可定量得到定域激子與電荷轉移激子在激發態的貢獻,更可以細節的得到各個單分子激發態與各個電荷轉移組態在雙分子激發態的貢獻大小。

在這篇論文中,我們利用量子化學方法,來定量研究電子與電洞在不同分子上之電荷轉移激子在最低兩個單態激發態貢獻的大小,這兩個單態激發態為兩個單分子的 1Bu 態分裂而成的。考慮這兩個單態激發態主要原因是相對於單分子情況,面對面聚集會使第一個單態激發態吸收強度明顯減弱而第二個單態激發態明顯增強¹²,產生電荷轉移激子易導致電荷分離至其他分子上而使放光效率減弱,雖然電荷轉移激子的產生會造成放光效率的減少,但在不同的應用上卻有正面的價值,例如在光二極體及太陽能電池的設計;相反的,了解電荷轉移激子的產生方式而加以抑制,可得到較佳的放光效率。

研究方法

分子結構的選擇方面,我們研究多稀鏈雙分子之聚集 (aggregation), 雙分子聚集方式為面對面 (face-to-face) 聚集,這樣的聚集是所謂的 H-aggregate。多烯分子的長度主要研究 2-30 units, 此處的 unit 指的是碳原子的數目,分子間的距離主要研究在 2.5-10 Å 之間,雙鍵與單鍵所使用的鍵長為 1.33Å 及 1.45Å。

雙分子聚集的激發態計算上,我們採用半經驗 PPP 模型並結合 MIM¹⁸ 以及 SCI¹⁹ 的方法。必須注意的是,這樣的半經驗方法計算並不是要得到量的精確預測而是希望以一系列量的變化得到共軛體系性質的趨勢。 PPP 模型下描述單一分子的分子軌域可表示為原子軌域的線性組合:

$$\Psi_n = \sum_{r} v_{n,r} \phi_r \quad (1)$$

ϕ_r 為在原子 r 上的 Pz 軌域, $v_{n,r}$ 為解自洽場方程式而得的展開係數,自洽場方程式以矩陣形式表示為:

$$\mathbf{F} \mathbf{v}_n = \mathbf{E}_n \mathbf{v}_n \quad (2)$$

其中 \mathbf{F} 為 Fock 哈密爾頓(Hamiltonian)矩陣, \mathbf{E}_n 為第 n 個分子軌域的能量, \mathbf{F} 的矩陣元可表示為:

$$F_{r,r} = \gamma_{r,r} - (1/2) P_{r,r} \gamma_{r,r} + \sum_s (P_{s,s} - Z_s) \gamma_{r,s} \quad (3)$$

$$F_{r,s} = h_{r,s} - (1/2) P_{r,s} \gamma_{r,s} \quad (4)$$

以上的下角標 r,s 代表不同原子的 Pz 軌域, $\gamma_{r,r}$ 為有效游離能(effective ionization energy), $h_{r,s}$ 為共振積分(resonance integral), $P_{r,s}$ 為鍵級(bond order), Z_s 為原子電荷(atomic charge), $\gamma_{r,s}$ 為電子排斥積分。以上這些原子軌域的積分

($h_{r,s}$ 為單電子積分, $\gamma_{r,s}$ 為雙電子積分)可利用有效核電荷(effective nuclear charge, Z),原子電荷,游離能,電子親合力來估計,但這樣傳統的估計法並不是非常方便,因此我們利用 Hida 提出的近似方法²⁰ 並調整參數,僅利用有效核電荷與原子電荷,即可估計這些積分。有效核電荷只需利用 Slater 規則計算而原子電荷則可由原子所提供的 Pz 軌域的電子數即可獲得,這樣的計算結果與利用實驗值計算結果幾乎相同,可參照表一。

單電子積分的估計方式為:

$$H_{r,r} = -\exp(0.342Z_r+0.555Z_r+0.758) \quad (5)$$

$$H_{r,s} = K S_{r,s}(R_{r,r} + R_{s,s}) \quad (6)$$

$H_{r,s}$ 是用 Wolfsberg-Helmholtz 方法來近似, K 為一常數 (=0.46) 而重疊積分

(overlap integral)估計方式為:

$$S_{r,s} = \exp(-0.1112R_{r,s}+0.1339)Z_rZ_s + (0.0449R_{r,s}-0.3759) (Z_r+Z_s) - 0.8627R_{r,s}+2.0631 \quad (7)$$

$R_{r,s}$ 為不同原子之間的距離。

雙電子積分的估計為:

$$\gamma_{r,r} = \exp(0.154Z_r+0.250Z_r+1.662)$$

(8)

$$\gamma_{r,s} = e^2/(R_{r,s}+f_{r,s}) \quad (9)$$

上式中 $\gamma_{r,s}$ 即所謂的Mataga-Nishimoto公式,其中 $f_{r,r} = e^2/\tilde{a}_{r,r}$, $f_{r,s} =$

$2f_{r,r}f_{s,s}/(f_{r,r}+f_{s,s})$ 。由以上的估計方式與傳統上的 PPP 模型有些不同,因為我們希望提高 PPP 模型的準確度而以較精確的方式估計單電子積分,利用參數方式估計所有原子間的重疊積分。以較複雜的方式將 Fock 矩陣計算出來,矩陣經由自洽場及正交化的過程可得到一組自洽場分子軌域,得到這組分子軌域可以用來建構不同的電子組態以進行分子激發態能量的計算。利用SCI方法對於單分子激發態的波函數可表示為單態單激發組態的線合:

$$\Phi_N = \sum C_{N,I} {}^1\Psi_I \quad (10)$$

因為一般分子處於單態基態,在假設自旋軌域耦合(spin-orbital coupling)不是很強時,由選擇率(selection rule)可知分子由光激發而產生的激發態也是單態,因此激發態波函數表示成單態組態的線性組合為合理的近似,我們考慮分子的所有單激發組態為基底組,其中單態組態 ${}^1\Psi_I$ 為 ${}^1\Psi_{i1 \rightarrow i2}$ 表示由自洽場分子軌域 $i1$ 躍遷到 $i2$, N 代表不同的激發態波函數,而其組態作用係數 $C_{N,I}$ 是由自洽場方法正交化組態作用矩陣而得,自洽場方程式可表示成:

$$S C_i = \Delta E_i C_i \quad (11)$$

ΔE_i 代表由基態激發至第 i 個激發態所需的能量,單激發組態作用矩陣 S 的矩陣元可表示成:

$$\begin{aligned} S_{I,I} &= \langle {}^1\Psi_{i1 \rightarrow i2} | H | {}^1\Psi_{i1 \rightarrow i2} \rangle - E_0 \\ &= E_2 - E_{i1} - \langle i_1 i_2 | i_1 i_2 \rangle + 2 \langle i_1 i_2 | i_2 i_1 \rangle \end{aligned} \quad (12)$$

$$S_{I,J} = - \langle i_2 j_1 | j_2 i_1 \rangle + 2 \langle i_2 j_1 | i_1 j_2 \rangle \quad (13)$$

E_0 為基態能量, E_{i1}, E_{i2} 為不同分子軌域能量

$$\langle ij|kl \rangle = \int \psi_i(1)\psi_j(2)(1/r_{12})\psi_k(1)\psi_l(2)dr_1dr_2 \quad (14)$$

上式可用(1)式展開加上 zero-differential overlap (ZDO) 的近似可簡化為:

$$\langle ij|kl \rangle = \sum_s V_{i,r}V_{j,s}V_{k,r}V_{l,s}\gamma_{r,s} \quad (15)$$

以上的方法可以計算單一分子激發能量,若將雙分子考慮成一個分子進行計算,則

此方法即為超分子近似方法。利用 MIM 方法,雙分子的組態作用矩陣可以表示為:

$$\mathbf{A} = \begin{array}{c} \begin{array}{cccc} {}^1\Psi_{aa, I, \dots} & {}^1\Psi_{bb, J, \dots} & {}^1\Psi_{ab, I', \dots} & {}^1\Psi_{ba, J', \dots} \\ \hline \mathbf{A}_{aa,aa} & \mathbf{A}_{aa,bb} & \mathbf{A}_{aa,ab} & \mathbf{A}_{aa,ba} \\ \hline \mathbf{A}_{bb,aa} & \mathbf{A}_{bb,bb} & \mathbf{A}_{bb,ab} & \mathbf{A}_{bb,ba} \\ \hline \mathbf{A}_{ab,aa} & \mathbf{A}_{ab,bb} & \mathbf{A}_{ab,ab} & \mathbf{A}_{ab,ba} \\ \hline \mathbf{A}_{ba,aa} & \mathbf{A}_{ba,bb} & \mathbf{A}_{ba,ab} & \mathbf{A}_{ba,ba} \end{array} \end{array}$$

此處 a,b 分別代表不同的分子而 I,J 代表不同區塊內的各種單激發組態, $\mathbf{A}_{aa,aa}$ 及

$\mathbf{A}_{bb,bb}$ 為單分子內躍遷的組態作用矩陣, $\mathbf{A}_{ab,ab}$ 及 $\mathbf{A}_{ba,ba}$ 為分子間的電荷轉移躍遷

的組態作用矩陣,其餘的為各種躍遷間的耦合矩陣, \mathbf{A} 的反對角線矩陣可表示為:

$$A_{I,J} = \delta_{j1i2}\sigma_{j2} - \delta_{j1i2}\sigma_{j2} - \langle j1i2 | i1j2 \rangle + 2 \langle j1i2 | j2i1 \rangle \quad (16)$$

$$\sigma_{j,q} = \sum_s V_{ip,r}V_{jq,s}\gamma_{r,s} \quad (17)$$

由(6)(17)式可知(16)式中的 σ 項來自於單分子間的波函數重疊。由單激發組態所

建構的矩陣 \mathbf{A} 並不包含基態的組態,因為由 Brillouin 理論可知單激發組態不會與

基態組態產生耦合。我們希望由單分子給出的訊息來獲得雙分子的特性,因此將

聚集時的定域化激發組態 $\mathbf{A}_{aa,aa}$ 及 $\mathbf{A}_{bb,bb}$ 利用自洽場與正交化,轉換成單分子的激

發態,這些激發態波函數可表示成定域化激發組態的線性組合。

$${}^1\Phi_{a_N} = \sum_{N,I} {}^1\Psi_{aa_I}, \quad {}^1\Phi_{b_M} = \sum_{M,J} {}^1\Psi_{bb_J}$$

(18)

經由轉換之後,組態作用矩陣 **A** 轉換成 **U**:矩陣 **U** 呈現出較明確的物理意義,如 **U^{ex}**

$$\begin{array}{c}
 {}^1\Psi_{a_N} \dots \quad {}^1\Psi_{b_M} \dots \quad {}^1\Psi_{ab_I} \dots \quad {}^1\Psi_{ba_J} \dots \\
 \mathbf{U} = \begin{array}{|c|c|c|c|}
 \hline
 \Delta \mathbf{E}^a & \mathbf{U}^{\text{ex}} & \mathbf{U}^{\text{loc},ct} & \\
 \hline
 \mathbf{U}^{\text{ex}} & \Delta \mathbf{E}^b & & \\
 \hline
 \mathbf{U}^{\text{ct},loc} & & \mathbf{U}^{ab,ab} & \mathbf{U}^{ab,ba} \\
 & & \mathbf{U}^{ba,ab} & \mathbf{U}^{ba,ba} \\
 \hline
 \end{array}
 \end{array}$$

為單分子激發態間的交互作用(在激子模型下,分子間的作用主要就是在估計 **U^{ex}**

的矩陣元),並且經由轉換後所得的矩陣 **U** 其所有矩陣元均可用單分子所計算出來

原子軌域係數及組態作用係數來計算,而非使用雙分子波函數的計算結果,這個方

法提供了一個方便的基底組以估計所有的矩陣元。 **U^{a,a}** 及 **U^{b,b}** 矩陣的對角線元可

由(11)(12)(13)(14)式獲得,矩陣 **U^{ab,ab}**, **U^{ba,ba}** 的對角線元可由(12)(14)式導出,其反

對角線元可由(14)(16)(17)式導出,其餘 **U** 的反對角矩陣的矩陣元可以從

(1)(14)(16)(17)(18)式導出。獲得了所有的矩陣元,最後將 **U** 正交化則可獲得雙分

子各個單態激發態中定域激子與電荷轉移激子所佔的比例。分子間不同的原子之

間的單電子積分與雙電子積分我們將延用單分子的估計法(6)(9)式獲得,這樣的

估計分子間積分值,單電子積分的量將會過小,因分子間 Pz 軌域是沿著 z 軸重疊,

當以分子內非 z 軸重疊方式估計,會導致分子間的作用較弱,而沒有去調整分子間

重疊積分的參數,是因為我們必須將 MIM 計算結果與超分子計算結果相比,以確

保尺度一致。我們發現,分子距離在 2Å 以內時,這兩種計算結果將發生非常大的

誤差,因此為確保計算方法上的穩定,我們所有計算分子距離為 2.5\AA 以上為主。

另外,理論上而言, Brillouin 理論將不適用於 U 矩陣,也就是說 U 矩陣與分子基態會有耦合產生,但是經由我們的計算結果發現,忽略這個耦合並不會出現明顯的誤差,因此我們將不額外計算這個耦合量。

結果與討論

一開始,我們變換不同的分子間距離以及變換不同的分子長度來獲得電荷轉移激子在雙分子第一個單態激發態上的貢獻,這一個單態激發態因其聚集的排列方式將使躍遷偶極矩(transition-dipole moment)很小以致吸收強度很弱。而由分子間距離與電荷轉移激子比例來觀察,見圖一,當多烯鏈的長度越短或分子間的距離減少時,電荷轉移激子的比例越高。分子長度夠短以及分子間距離夠近時,如多烯分子為 4 units 時,當分子間距離小於 3.2\AA 時,第一個單態激發態以電荷轉移激子為主。當分子間的距離超過 4\AA ,電荷轉移激子的貢獻幾乎消失,此時雙分子的第一個激發態幾乎全為定域激子的貢獻,而隨著分子間的距離增加將接近於單一分子的結果。另外長度的增加伴隨的電荷轉移激子變化量趨於定值。

第二個單態激發態與第一個單態激發態有很大的不同,其聚集方式可以使躍遷偶極矩很大以致吸收強度很強。由圖二可發現,第二個單態激發態的電荷轉移激子分布的範圍較第一個單態激發態廣。而以電荷轉移激子隨分子間長度變化方式而言,第二個單態激發態與第一個單態激發態類似,電荷轉移激子的比例隨著長

度或分子間距離減少而增加,特別值得注意的是第二個單態激發態中多烯鏈長小於 24 units 時,均在某特定長度內出現異常高比例的電荷轉移激子(>90%)且有極大值出現。由圖三,可以明顯看到極大值的出現且有分子長度越長出現位置在越短之相反關係。為了要了解圖一與圖二的現象,我們先將定域激子與電荷轉移激子之間的作用力不考慮,即 $U^{loc,ct}=0$ (分子間的 $U=0$),由圖四(a),第一個單態激發態隨著多烯鏈長度增加電荷轉移激子出現位置減少的變化,在長度超過 12 units 時,第一個單態激發態為定域激子的貢獻,可對應到圖一。分子長度為 4 units 時,在分子間距離小於 3.25\AA , 電荷轉移激子明顯為第一個單態激發態的主要貢獻。而分子長度為 8 units 時,分子間距離小於 2.75\AA 此時定域激子與電荷轉移激子能量接近(可由 12 units 電荷轉移激子特徵消失看出)。互相間的作用力使定域激子與電荷轉移激子所佔的比例約相同。比較圖四(b),呈現出第二個單態激發態的電荷轉移激子分佈較第一個單態激發態廣,可對應圖二電荷轉移激子比例急劇下降的位置非常吻合。綜合上述,可以解釋圖一,圖二多烯鏈的長度或分子間的距離減少時,電荷轉移激子的比例越高的趨勢,主要為定域激子與電荷轉移激子能量間的競爭,而兩者之間的交互作用力非決定此趨勢的主因。為了更進一步了解此一趨勢,我們使單分子的定域激子間的作用力 $U^{ex}=0$ 可以發現雙分子的第一個單態激發態與第二個單態激發態能量相同且電荷轉移激子下降的位置均較圖四(b)第二個單態激發態左移 0.5\AA 。此處計算的範圍在 4-28 units 之間,因此單分子的定域化單態激發態間的作用力 U^{ex} 對雙分子第一個單態激發態的

電荷轉移激子的出現較不利而對第二個單態激發態較有利,且對第一個單態激發態的影響較大。為了更深入了解定域激子與電荷轉移激子競爭效應的原因,以及圖二出現極大值的來源,我們計算 2 units 的多烯分子,此分子各分區矩陣的矩陣元均只有一個,可得更進一步簡化。當我們忽略反對角線元素,可得圖五,隨著距離的減少電荷轉移激子的能量減少,但定域激子部分不變。當分子間距離小於 4\AA 時,電荷轉移激子的能量較定域激子小,此原因為定域激子與電荷轉移激子之電子交換能 (exchange energy) 的不同, (12)式的最後一項即為電子交換能。當我們計算的單分子的各個單態激發態時包含此能量,而分子間電荷轉移激子的電子交換能化成原子軌域的數學形式時,將牽涉到雙中心以上的原子軌域積分,因 PPP model 使用 zero-differential overlap (ZDO)的近似而使這些貢獻為零,一般而言 ZDO 這樣的近似方法是成功的,因此我們可以明確解釋圖三的趨勢主要來源是單分子之定域化單態激發態間的交互作用(U^{ex})及定域激子與電荷轉移激子之間的電子交換能的差異所造成。另外由圖六,所有非對角線上的矩陣, $U^{a,ab}$ 此耦合效應較小,忽略時不會影響整個趨勢,其餘耦合隨著距離增加而減少,比較圖五,電荷轉移激子隨著距離的增加而增加。這樣相反的趨勢,在適當的分子長度,將在我們討論的分子間距離範圍內出現極大值。

結 語

多烯鏈的研究顯示,最低能量的兩個單態激發態均有長度或距離減少時,電荷

轉移激子比例增加的趨勢。這和一般激子在共軛長度越長的分子上電荷轉移激子越少的概念一致,我們更進一步定量說明當分子長度與分子間距離達適當比例時,單態激發態會以電荷轉移激子為主且第二個單態激發態較第一個單態激發態有明顯的不同,其在共軛長度較短分子有明顯大範圍高比例的電荷轉移激子產生;而相對於第一個單態激發態高比例的主要決定因素為單分子定域激子間的交互作用及定域激子與電荷轉移激子之電子交換能差異。在這些高比例的電荷轉移激子隨著不同分子間距離的變化會產生極大值,極大值的位置隨著分子長度減少而增加,其原因為主要的激子耦合隨距離增加而減少,但電荷轉移激子能量隨距離增加而增加,因此會出現極大值,而第一個單態激發態若要產生極大值則需要更接近的分子距離($<2.5\text{\AA}$)。經由以上的討論我們知道想要獲得較高比例的電荷轉移激子所需要尋找的方向,例如因為控制分子間的距離不是很容易所以找尋較短的共軛分子或者尋找共軛分子有較大的電子交換能,可能獲得電荷轉移激子在較遠的分子距離有明顯的貢獻。另外,我們研究多稀分子面對面堆積,當分子長度短的情況下,其基態與第二個單態激發態的躍遷很強同時電荷轉移激子的比例在分子距離較長的位置有明顯的貢獻,這樣的性質將會有利於光轉換成電的效率。

參考文獻

1. Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D.; Stocking, A. *Science* **1996**, *273*, 884.

2. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
3. Pei, Q.; Yu, C.; Zhang, Y.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086.
4. Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684.
5. Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *268*, 270.
6. Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478.
7. Yu, G.; Wang, J.; McElvain, J.; Heeger, A. J. *Adv. Mater.* **1998**, *17*, 1431.
8. Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15
9. Hide, F.; Diaz-Garcia, M. A.; Schwartz, B.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Science* **1996**, *273*, 1833.
10. Friend, R. H.; Burroughes, J.; Shimoda, T. *Phys. World* **1999**, June, 35.
11. Shaheen, S. E.; Jabbour, G. E.; Kippelen, B.; Peyghambarian, N.; Anderson, J. D.; Marder, S. R.; Armstrong, N. R.; Bellmann, E.; Grubbs, R. H. *Appl. Phys. Lett.* **1999**, *74*, 3212.
12. Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*, Oxford University Press, New York 1999.
13. Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765.
14. Yan, M.; Rothberg, L. J.; Kwock, E. K.; Miller, T. M. *Phys. Rev. Lett.* **1995**, *75*, 1992.
15. Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Gobel, E. O.; Müllen, K.; Bässler, H. *Chem. Phys. Lett.* **1995**, *240*, 373.
16. Samuel, I. D. W.; Rumbles, G.; Collison, C. J. *Phys. Rev. B* **1995**, *52*, 11573.

17. Levine, I. N. *Quantum Chemistry*, Prentice Hall: New Jersey, 2000
18. Warshel, A.; Parson, W. W. *J. Am. Chem. Soc.* **1987**, *109*, 6143
19. Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*, MacMillan: New York, 1982.
20. Hida, M. *Dyes and Pigments.* **1995**, *28*, 217

附件一

Self-Organization of Triple-Stranded Carbon

Nanoropes

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Novel self-organized carbon nanoropes consisting of three helically coiled multi-wall nanotubes with a remarkable constant pitch over several microns were grown by the lanthanide oxide-catalyzed decomposition of gaseous acetylene on aluminophosphate (AlPO₄-5) support. Direct characterization by the stereo transmission electron microscope and scanning electron microscope has convincingly shown that these three strands entwine with each other helically, which are presumably kept together by both the spontaneous curvature and van der Waals (vdW) attraction.

Recently, there has been intensive interest in the structure and morphology of carbon nanofibers prepared by the catalytic decomposition of gaseous hydrocarbon using various transition metals such as iron, cobalt, nickel, and some of their alloys (1-5). These nanofibers were generally whisker-like tubular structures with diameters controlled by the size of the small metal particles. In addition to the straight tubes, several intricate shapes and structures including helices, cones, tori and rings have been identified (6-10). At higher structural level, strong inter-tube van der Waals (vdW) attraction can generate at least two kinds of self-organization among nanotubes: firstly, nanotubes can bunch together and leads to the rope formation (10); secondly, upon the ultrasonic irradiation, the nanotubes may be self-folded into ring

configurations (11) and stabilized by vdW attractions. However, to our knowledge, no observation of the self-organization among helically coiled nanotubes has been reported yet. In this work, we report for the first time the preparation and characterization of the novel triple-stranded helically coiled carbon nanoropes by the high-temperature decomposition of gaseous acetylene via the microporous aluminophosphate ($\text{AlPO}_4\text{-5}$) support (12, 13) and rare earth metal oxide (Pr_6O_{11}) as the catalyst. The microstructure and composition of the nanoropes were characterized by transmission electron microscope (TEM), scanning electron microscope (SEM), energy dispersive X-ray (EDX), and selective area diffraction (SAD).

The triple-stranded carbon nanoropes were synthesized using the $\text{AlPO}_4\text{-5}$ supported Pr_6O_{11} catalyst, which was prepared by the impregnation method. 0.1 g Pr_6O_{11} fine powder was dissolved in 10 ml distilled water and stirred for 10 min at 343 K. One gram of microporous $\text{AlPO}_4\text{-5}$ with the template was then slowly added into the solution. The mixture was ground to fine grey powder (100 mesh) after drying in an oven at 393 K for 8 hours, and the resulting catalyst was used immediately. A ceramic boat containing 100 mg of catalyst was placed inside a quartz tube located in the central part of a tubular electric furnace. The catalyst was heated at a rate of 30 K/min from room temperature to 473 K in air and retained at 473 K for 3 hours. The gas mixture ($\text{N}_2 = 100$ ml/min, $\text{C}_2\text{H}_2 = 10$ ml/min) was introduced for about 3 minutes before the sample was brought to the desired reaction temperature (973 K) at a rate of 30 K/min, and the reaction was allowed to proceed at 973 K for another 2 hours. Afterward, the acetylene gas flow was stopped, and the reactor was cooled down to room temperature in flowing nitrogen (100 ml/min) for 14 hours. The reaction product was finally collected as fine black powder from the ceramic boat. The microstructure of carbon nanoropes was studied with the aid of TEM (Hitachi H-7100, 120 kV and JEOL JEM-2010, 200 kV, equipped with ISIS 300 Energy Dispersive X-ray analyzer) and SEM (Hitachi S5000, 20 kV) after sonicating the

samples in ethanol for 1 hour and dispersing a drop of solution over holey carbon grids.

The product prepared by this method was found to contain large numbers of irregularly curved nanofilaments with various complicated shapes and forms (Fig. 1). Among these nanofilaments, the most striking finding was that the nanoropes, as shown in area A and B of Fig. 1, appeared to consist of three helices entwining with each other. A rough estimation from these nanoropes we have found that the width of each strand is about 10 to 30 nm. The pitches and diameters for the triple helices vary significantly. An analysis showing the distribution of pitches and diameters of many TEM images is summarized in Fig. 2 where the solid line depicts the theoretical prediction of the optimal ratio of pitch (p) and diameter ($2r$) for a single-stranded helix (14). Therefore, it is convenient to distinguish triple-stranded nanoropes according to the ratio of their pitch and diameter, or equivalently, the pitch angle of the helix, $\phi = \arctan(p/2r)$. The computer graphs in Fig. 2 are three representative model structures for type I ($\phi < 45^\circ$), optimal ($\phi = 45^\circ$) and type II ($\phi > 45^\circ$) triple-stranded nanoropes with the same arc-length for the central lines, respectively. The pitch and diameter of a typical type I nanorope as shown in Fig. 3 are found to be 140 nm and 80 nm, respectively, which leads to $p/2r \approx 1.8$ ($\phi = 30^\circ$). Type II nanorope such as the representative one in Fig. 4 has a high pitch angle with a larger ratio, $p/2r \approx 4$ ($\phi = 52^\circ$).

The pitches and diameters of the triple helices of both types are relatively uniform throughout the total length of the nanoropes ranging from 1 to 10 μ m. The number of repeated units in a triple helix can be as high as about 40 units, despite the fact that the detailed conformation for each pitch (Fig. 3) still shows some minor fluctuations. These small fluctuations in triple-stranded carbon nanoropes might originate from the intrinsic curvature associated with the growth. The intrinsic curvature, however, has a stronger influence on the morphology of the single-stranded filaments, e.g. carbon filaments in area C of Fig. 1. Hence, the entropic effect

dominates in the growth of single-stranded carbon filaments and results in conformation disorder with many complicated shapes. Unlike the single-stranded filaments, the existence of strong non-directional vdW interaction between tubes in the triple-stranded nanoropes may have important implications for their geometry, thermodynamic stability, and formation mechanism. As can be seen in Fig. 2, most of the triple helices belong to type I nanoropes with low pitch angles. Since the low pitch triple helices appear to have larger vdW adhesive energy due to larger contact area among different strands, it is proposed that the vdW adhesive energy is the major factor for the stability of triple-stranded nanorope. However, additional work will be necessary for a detailed understanding of the underlying physics.

It should be noted that the synthesis of triple helices is quite sensitive to the reaction temperature. Only within a narrow temperature range from 968 K to 978 K have the triple-stranded coils been observed by the current method of preparation. In addition to the temperature effect, the existence of the template (TEA, triethylamine) in the zeolite is also critical for the growth of triple helices. No triple helix has been found when the template in the zeolite support is removed. This suggests that the thermal decomposition of the template in the zeolite may play a subtle role in the formation of the nanofilaments with size large enough to form the triple helices. However, within the detection limit of approximately 1%, the EDX analysis in TEM indicated that the nanoropes contain neither trace of rare earth metal Pr nor nitrogen element. It is also confirmed from the SAD data that there is no inclusive Pr crystal in the nanoropes.

The contrast in TEM depends on the number of electrons scattered: the more atoms are in a region, the higher is the contrast. The images obtained from TEM are close to the 2-D projections of the viewed objects, while there are also contributions from out of focus regions. Another possible structure, which may give rise to a similar TEM image as in Fig. 3, is a triple-stranded braid, since both the triple-stranded helix and the triple-stranded braid exhibit a similar 2-D projection. Therefore, the SEM and

stereo TEM were chosen to distinguish these two possible 3-D structures. Fig. 5 shows the SEM micrograph of an individual type I nanorope with a pitch angle about 25° . The SEM micrograph was taken with an electron microscope operated at 20 kV. The greater depth of field of SEM provides much more information about the three-dimensional structure of the nanoropes. In fact, the micrograph in Fig. 5 indicates that the nanorope is a left-handed triple-stranded helix. This 3-D structure is also confirmed by the stereo TEM techniques, where two TEM stereograms with a tilted angle 7° apart were taken for the nanorope in Fig. 3. The 3-D appearance of the sample object can be observed by superimposing the stereo pair, and thus visualize the relative depths of three strands in the nanorope. In conclusion, both types of techniques have shown that the entwisting nanoropes are indeed triple-stranded helices instead of braids, which is consistent with the fact that we didn't observe the existence of side view of a braid in all TEM images. However, the possibility of forming carbon nanobraids cannot be completely excluded. Using the stereo TEM and SEM, we were also able to identify some right-handed triple helices in addition to the left-handed ones. This indicates that the nanoropes are a racemic mixture of two chiral forms.

References and Notes

1. M. S. Dresselhaus, *et al.*, *Graphite Fibers and Filaments, Springer Series in Materials Science 5* (Springer-Verlag, New York, 1988).
2. M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science and Technology of Fullerenes and Carbon Nanotubes*, (Academic Press, San Diego, 1996).
3. N. M. Rodriguez, *J. Mater. Res.* **8**, 3233-3250 (1993).
4. R. T. Baker, *Carbon* **27**, 315-323 (1989).
5. M. Endo *et al.*, *J. Phys. Chem. Solids* **54**, 1841-1848 (1993).

6. S. Amelinckx *et al.*, *Science* **265**, 635-639 (1994).
7. R. Gao, Z.-L. Wang, and S. Fan, *J. Phys. Chem.* **104**, 1227-1234 (2000).
8. A. Fonseca *et al.*, *Synthetic Metals* **77**, 235-242 (1996).
9. X. B. Zhang *et al.*, *Europhys. Lett.* **27**, 141-146 (1994).
10. A. Thess, *et al.* *Science* **273**, 483-487 (1996).
11. R. Martel, H. R. Shea, and P. Avouris, *J. Phys. Chem. B* **103**, 7551-7556 (1999).
12. B. M. Lok *et al.*, US Patent No. 4440871, 1984.
13. H. D. Sun, Z. K. Tang, J. Chen, and G. Li, *Applied Physics A* **69**, 381-384 (1999).
14. Z.-C. Ou-Yang, Z.-B. Su, and C.-L. Wang, *Phys. Rev. Lett.* **78**, 4055-4058 (1997).
15. The three central lines of a model structure for an ideal theoretical triple helix can be described parametrically by the 3-D coordinate: $\{\mathbf{a}_i(t) = (r\cos(\omega t_i + \zeta_i), r\sin(\omega t_i + \zeta_i), \rho t_i/2\delta), i = 1, 2, 3\}$, and the phases are $\zeta_i = 0, 2\delta/3, 4\delta/3$, respectively. Tube surfaces around the central lines are given by $\mathbf{Y}(t, \epsilon) = \mathbf{a}(t) + r_0 [\mathbf{N}(t) \cos \epsilon + \mathbf{B}(t) \sin \epsilon]$, where $\mathbf{N}(t)$ is the normal vector and $\mathbf{B}(t)$ is the binormal vector along the central line of the tube surface, and r_0 is the width of the tube.

Supplementary information is available on *Nature's* World-Wide Web site (<http://www.nature.com>) or as paper copy from the London editorial office of *Nature*.

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Figure legends

Figure 1. A typical TEM figure showing three types of carbon nanofilaments grown by the lanthanide oxide-catalyzed decomposition of acetylene on the $\text{AlPO}_4\text{-5}$ support. Type I and II carbon nanoropes are marked as A and B, respectively. Carbon filaments in the area C mainly consist of irregularly curved single-stranded carbon nanotubes with an average width about 10 nm. White area in the figure is a mixture of carbon black and $\text{AlPO}_4\text{-5}$ zeolite.

Figure 2. Pitch versus diameter of triple-stranded carbon helices. The dots in the figure stand for the measurements of pitch as a function of diameter of typical nanoropes observed in the current work. The solid line corresponds to the optimal ratio of pitch and diameter ($p/2r=\delta$, or $\delta=45^\circ$) for single-stranded helices in the absence of vdW interaction predicted theoretically by Ou-Yang *et al.* (14). The computer graphs in the figure are three representative model structures for type I, type II and optimal triple-stranded nanoropes with the same arc-length for the central lines, respectively (15). Most of triple helices observed belongs to type I nanorope with low pitch angle, indicating that it is easier to grow low pitch triple-stranded helices.

Figure 3. The TEM micrograph for typical type I nanoropes. The pitch and diameter for the nanorope in the figure are about 140 nm and 80 nm, respectively, which leads to a low $p/2r$ ratio about 1.8 ($\delta = 30^\circ$).

Figure 4. The TEM image for the representative type II nanorope. The pitch and the diameter are about 480 nm and 120 nm, respectively, which leads to a large ratio ($p/2r \approx 4$) and a high pitch angle ($\delta \approx 52^\circ$).

Figure 5. The SEM micrograph of an individual type I nanorope. The pitch and the diameter are about 150 nm and 110 nm, respectively, which leads to a low pitch ratio about 1.36. The SEM micrograph was taken with an electron microscope operated at 20 kV.

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Fig. 5