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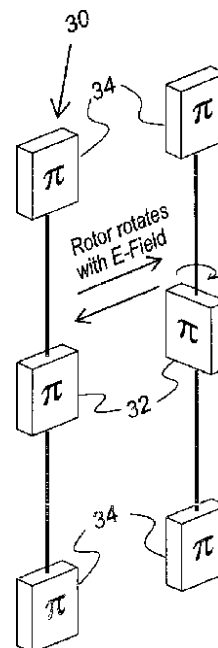
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(54) 【発明の名称】 電子スイッチング、ゲーティング及びメモリ用途の、電界によって駆動する中央回転部を有する
 双安定分子メカニカルデバイス

(57) 【要約】

クロスワイヤデバイス、即ち分子システム (30) が接続ユニットによって接続されている一対の電極、のような電界駆動スイッチ用の分子システム (30) を提供する。前記クロスワイヤデバイスは、一方のワイヤが他方と 0° 以外の角度で交差する接合部を形成する一対の交差したワイヤと、前記接合部において前記一対の交差したワイヤを接続する少なくとも 1 つのコネクタ種とから構成される。前記コネクタ種は、固定部 (固定子) (34) 間に回転部 (回転子) (32) が接続されている分子システム (30) の回転子/固定子構造に基づく分子配座変化によって電界誘導バンドギャップ変化を起こし、それ故導電率の変化する分子システム (30) からなる。従って、それらを容易に組み合わせることで、記憶、論理及び通信機能をもたらすクロスバー回路を形成できるナノメートルスケールの可逆電子スイッチを提供する。

【選択図】 図2



【特許請求の範囲】

【請求項 1】

一対の電極（12、14）によって生成される電界内で構成され、前記電極に電氣的に接続されている分子システム（30）からなる双安定分子メカニカルデバイス（60）であって、前記分子システム（30）が2つの固定子部（34）間に接続されている1つの回転子部（32）を有し、該回転子部（32）が前記電界の印加によって前記固定子部（34）に関して少なくとも2つの異なる状態間で回転し、それによって前記分子システム（30）内のバンドギャップ変化が引き起こされ、第1の状態では前記分子システム（30）の少なくとも大部分にわたって拡張共役が存在し、その結果バンドギャップが比較的小さくなり、第2の状態では前記拡張共役が破壊され、その結果バンドギャップが比較的大きくなる双安定分子メカニカルデバイス（60）。

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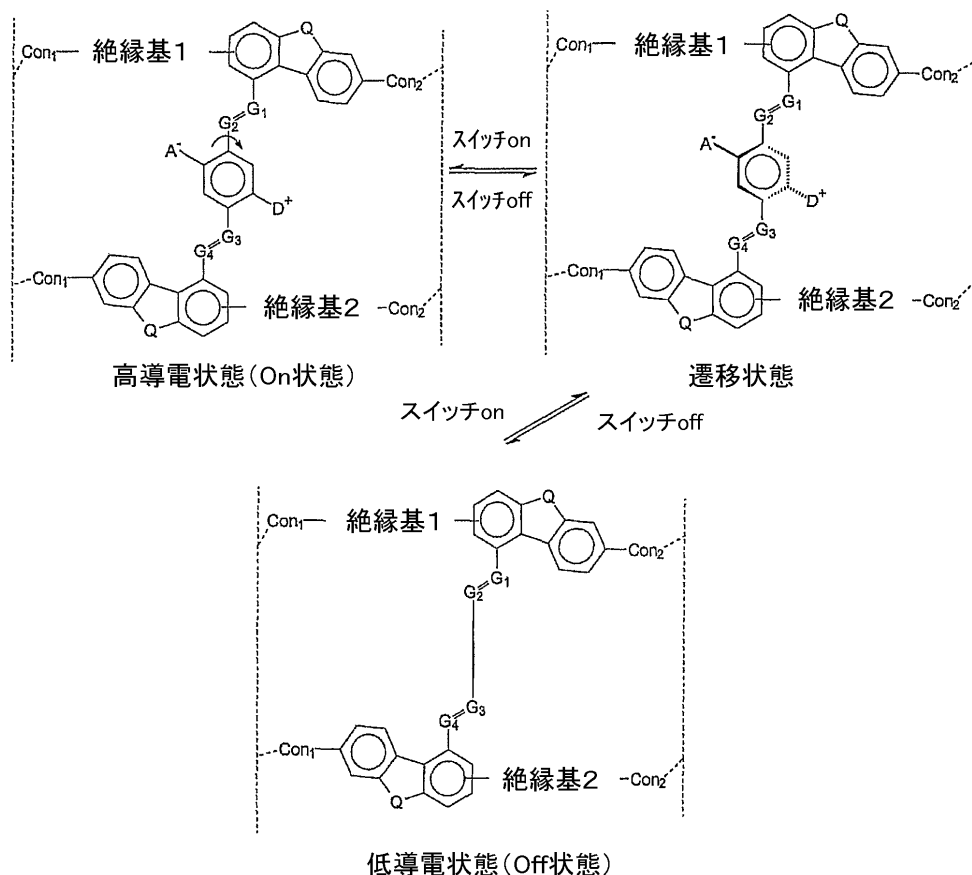
【請求項 2】

前記分子システム（30）が方位軸を有し、前記外部電界が前記方位軸に対して平行に印加される場合に、前記回転子部（32）が前記方位軸に対して垂直に配向する請求項1に記載の分子デバイス（60）。

【請求項 3】

前記分子システム（30）が、

【化 1】



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からなる請求項2に記載の分子デバイス（60）。

ここで、

A^- は、（a）水素、（b）カルボン酸及びその誘導体、（c）硫酸及びその誘導体、（d）リン酸及びその誘導体、（e）ニトロ、（f）ニトリル、（g）N、O、S、P、F、Cl及びBrからなる群から選択されるヘテロ原子、（h）前記ヘテロ原子のうちの少なくとも1つを有する官能基、（i）飽和あるいは不飽和炭化水素、及び（j）置換炭化水素、からなる群から選択される電子求引基からなる受容基であり、

D^+ は、（a）水素、（b）アミン、（c）OH、（d）SH、（e）エーテル、（f）

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飽和あるいは不飽和炭化水素、(h)置換炭化水素、及び(i)B、Si、N、O、S、P及びIからなる群から選択されるヘテロ原子のうちの少なくとも1つを有する官能基、からなる群から選択される電子供与基からなる供与基であって、前記受容基よりも電気的陽性が高い供与基であり、

C_{on1}及びC_{on2}は、分子と、金属電極、無機基材及び有機基材からなる群から選択される固体基材との間の接続ユニットであって、(a)水素(水素結合を利用する)、(b)C、N、O、S及びPからなる群から選択される多価ヘテロ原子、(c)前記ヘテロ原子を含む官能基、(d)飽和あるいは不飽和炭化水素、及び(d)置換炭化水素、からなる群から独立して選択される接続ユニットであり、

G₁、G₂、G₃及びG₄は、所望の電子特性を得るために、前記固定子を前記各回転子に接続するか、又は2つ以上の共役環を接続するブリッジング基であって、(a)N、O、S及びPからなる群から選択されるヘテロ原子、(b)前記ヘテロ原子のうちの少なくとも1つを有する官能基、(c)飽和あるいは不飽和炭化水素、(d)置換炭化水素、(e)単原子ブリッジ、及び(f)前記回転子と前記各固定子間の直接シグマ結合、からなる群から選択されるブリッジング基であり、

Qは、2つのフェニル環間の接続ユニットであって、(a)S、(b)O、(c)NH、(d)NR、(e)炭化水素、及び(f)置換炭化水素、からなる群から選択される接続ユニットであり、

垂直方向の点線は、前記分子が電気的に接続されている前記固体基材を表す。

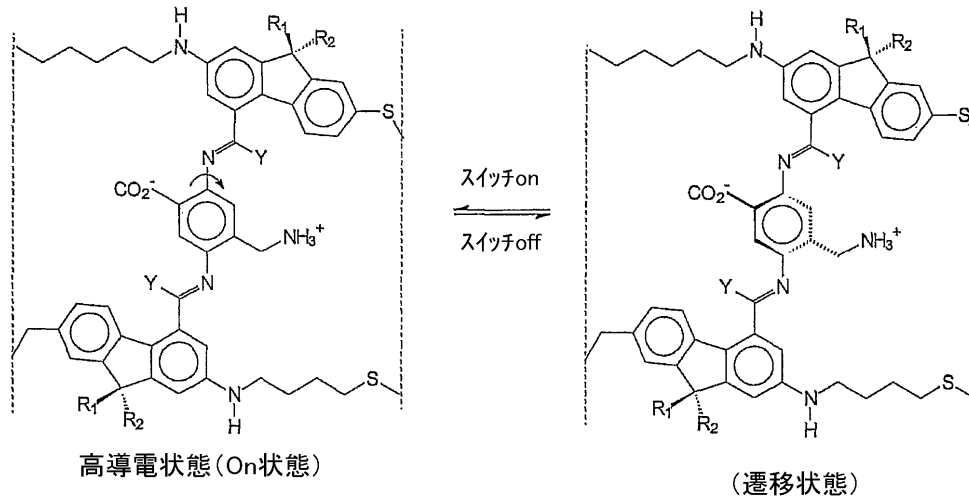
【請求項4】

前記分子システム(30)が、

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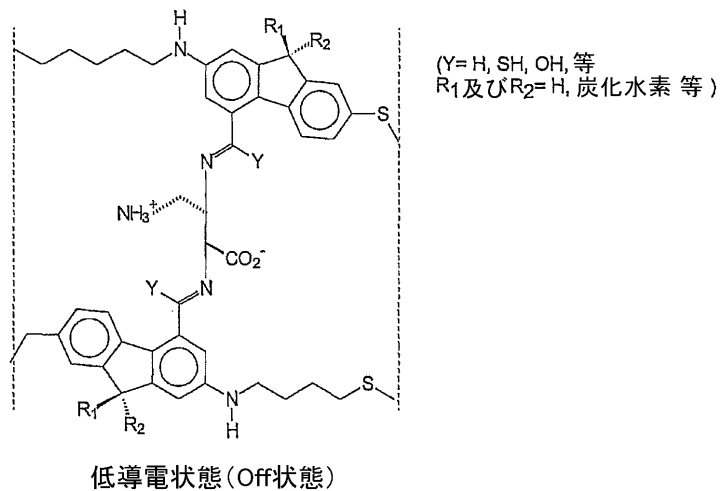
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【化 2】



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スイッチon
スイッチoff



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からなる請求項 3 に記載の分子デバイス (60)。

ここで、

R₁ 及び R₂ は、それぞれ独立して水素あるいは炭化水素であり、

Y は、水素、OH 及び SH からなる群から選択されている。

【請求項 5】

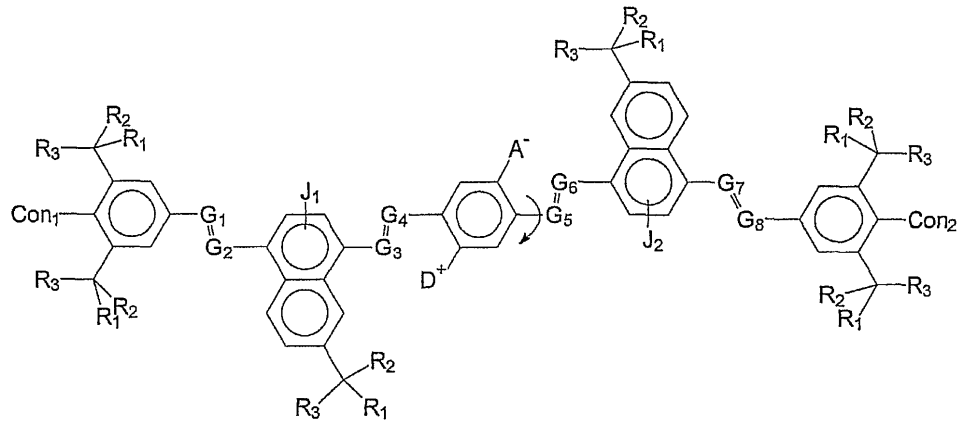
前記分子システム (30) が方位軸を有しており、前記外部電界が前記方位軸に対して垂直に印加される場合に、前記回転子部 (32) が前記方位軸に対して平行に配向する請求項 1 に記載の分子デバイス (60)。

【請求項 6】

前記分子システム (30) が、

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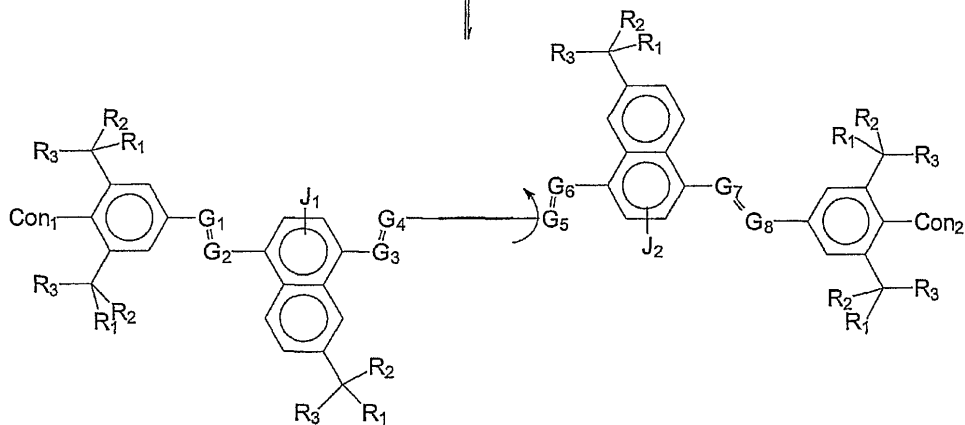
【化 3】



On状態(高導電状態)

スイッチOn

スイッチOff



Off 状態(低導電状態)

からなる請求項 5 に記載の分子デバイス (60)。

ここで、

A^- は、(a) 水素、(b) カルボン酸及びその誘導体、(c) 硫酸及びその誘導体、(d) リン酸及びその誘導体、(e) ニトロ、(f) ニトリル、(g) N、O、S、P、F、Cl 及び Br からなる群から選択されるヘテロ原子、(h) 前記ヘテロ原子のうちの少なくとも 1 つを有する官能基、(i) 飽和あるいは不飽和炭化水素、及び (j) 置換炭化水素、からなる群から選択される電子求引基からなる受容基であり、

D^+ は、(a) 水素、(b) アミン、(c) OH、(d) SH、(e) エーテル、(f) 飽和あるいは不飽和炭化水素、(h) 置換炭化水素、及び (i) B、Si、N、O、S、P 及び I からなる群から選択されるヘテロ原子のうちの少なくとも 1 つを有する官能基、からなる群から選択される電子供与基からなる供与基であって、前記受容基よりも電気的陽性が高い供与基であり、

Con_1 及び Con_2 は、ある分子と他の分子、又は分子と、金属電極、無機基材及び有機基材からなる群から選択される固体基材との間の接続ユニットであって、(a) 水素 (水素結合を利用する)、(b) C、N、O、S 及び P からなる群から選択される多価ヘテロ原子、(c) 前記ヘテロ原子を含む官能基、(d) 飽和あるいは不飽和炭化水素、及び (d) 置換炭化水素、からなる群から独立して選択される接続ユニットであり、

R_1 、 R_2 及び R_3 は、前記各回転子のための回転の空間を設けながら、分子が密集でき

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るようにする適切な 3 次元の枠組みを設けるためのスペーシング基であって、(a) 水素、(b) 飽和あるいは不飽和炭化水素、及び (c) 置換炭化水素、からなる群から選択されるスペーシング基であり、

G_1 、 G_2 、 G_3 、 G_4 、 G_5 、 G_6 、 G_7 及び G_8 は、所望の電子特性を得るために、前記固定子を前記各回転子に接続するか、又は 2 つ以上の共役環を接続するブリッジング基であって、(a) N、O、S 及び P からなる群から選択されるヘテロ原子、(b) 前記ヘテロ原子のうちの少なくとも 1 つを有する官能基、(c) 飽和あるいは不飽和炭化水素、(d) 置換炭化水素、(e) 単原子ブリッジ、及び (f) 前記回転子と前記各固定子間の直接シグマ結合、からなる群から選択されるブリッジング基であり、

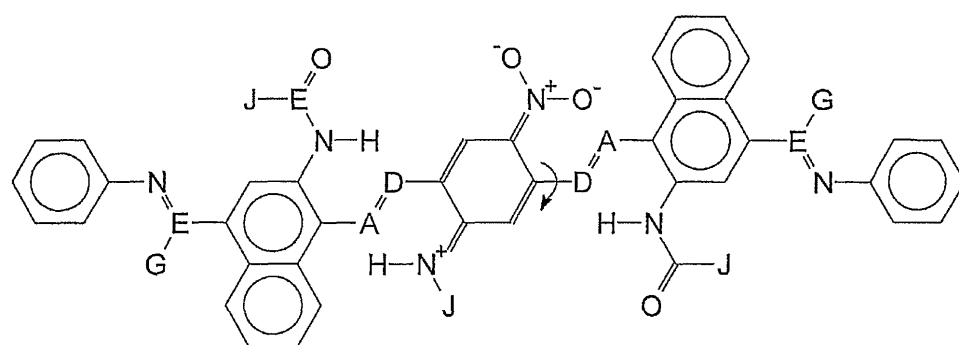
J_1 及び J_2 は、誘導性効果、共鳴効果及び立体効果からなる群から選択される少なくとも 1 つの適切な機能的効果をもたらすための調整基であって、(a) 水素、(b) N、O、S、P、B、F、Cl、Br 及び I からなる群から選択されるヘテロ原子、(c) 前記ヘテロ原子のうちの少なくとも 1 つを有する官能基、(d) 飽和あるいは不飽和炭化水素、及び (e) 置換炭化水素、からなる群から選択される調整基である。

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【請求項 7】

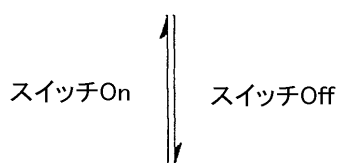
前記分子システム (30) が、

【化 4】

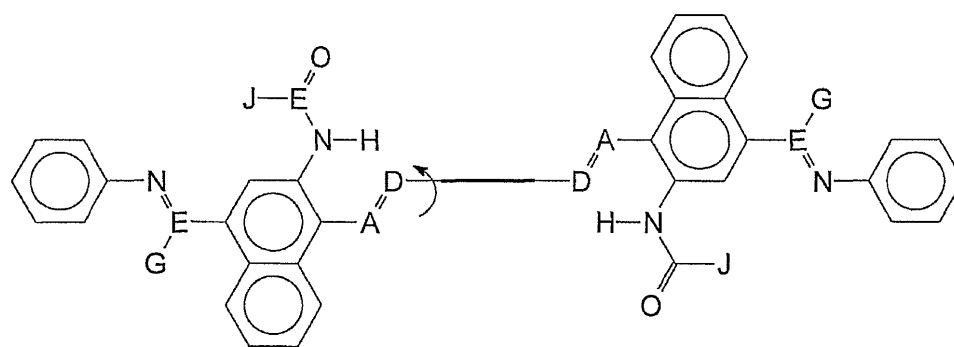


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高導電状態 (On 状態)



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低導電状態 (Off 状態)

からなる請求項 6 に記載の分子デバイス (60)。

ここで、

文字 A、D、E、G 及び J は、前記分子システムの幾何学的構造及び光学的特性を調整するために、種々の化学ユニットを利用することができる部位を示しており、一般的に A、

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D、E、G及びJは、ヘテロ原子、炭化水素（飽和あるいは不飽和のいずれか）、及び少なくとも1つの前記ヘテロ原子を有する炭化水素、からなる群から独立して選択され、上記に加えて、文字G及びJは、水素、F、C l、B r及びIからなる群から独立して選択される。

【請求項8】

1つのワイヤ（14）が他のワイヤ（12）と0°以外の角度で交差する接合部（18）を形成する一对の交差したワイヤ（12、14）と、前記接合部（18）において前記一对の交差したワイヤを接続させる少なくとも1つのコネクタ種（16）とを含むクロスワイヤデバイス（10）からなる分子デバイス（60）であって、前記接合部（18）がナノメートル単位の機能寸法を有し、前記少なくとも1つのコネクタ種（16）が前記分子システム（30）からなる請求項1に記載の分子デバイス（60）。 10

【請求項9】

前記クロスワイヤデバイス（10）が、記憶装置、論理装置、マルチプレクサ、デマルチプレクサ、集積回路に適合性のあるインターコネクト機器、フィールドプログラマブルゲートアレイ（FPGA）、クロスバースイッチ、及び通信装置から成る群から選択される請求項8に記載の分子デバイス（60）。

【請求項10】

前記分子システム（30）が、接続ユニットによって前記一对の電極（12、14）に接続されている請求項1に記載の分子デバイス。

【請求項11】

請求項1の分子システム（30）を包含する双安定分子システム（30）。 20

【発明の詳細な説明】

【技術分野】

【0001】

本発明は、概して、その機能長スケールがナノメートル単位である電子デバイスに関し、より詳細には、電子スイッチングをもたらす種類の分子に関する。マイクロメートル（ μm ）及びナノメートル（ nm ）の両スケールの電子デバイスを、本明細書における教示に従って構成することができる。

【背景技術】

【0002】

分子エレクトロニクス分野は初期の段階にある。現在までに、電子スイッチのような分子に関して技術文献で公開されたものとしては、2つの説得力ある論証がある。C. P. Collierらによる Science、Vol. 285、pp. 391-394（1999年7月16日）及びC. P. Collierらによる Science、Vol. 289、pp. 1172-1175（2000年8月18日）を参照されたい。しかし、本話題をとりまく科学的コミュニティ内では、多数の思い入れと関心が存在する。公表された研究においては、ロタキサン又はカテナンと呼ばれる分子を2つの金属電極間にトラップし、その分子の両端に正のバイアスをかけることによってON状態からOFF状態へ切り替えさせていた。ロタキサン及びカテナンに関しては、ON状態及びOFF状態で、その抵抗率が、それぞれ、ファクターでおよそ100及び5と異なっていた。 30 40

【0003】

ロタキサンに関する主な問題は、それが不可逆的なスイッチであるということであった。それは一度だけ切り替えることができるものである。従って、プログラマブル読み出し専用記憶装置（PROM）には利用できるが、ROM類似デバイスにおいて、又はフォールトトレラント通信及び論理ネットワークのような再構成可能システムにおいては用いることができない。さらに、ロタキサンは、スイッチを切り換える前に、酸化及び／又は還元反応を起こす必要がある。このことは、スイッチを切り換えるのに、相当な量のエネルギーの消耗を要する。加えて、ロタキサン分子及び同族化合物の大きく且つ複雑な特性は、分子のスイッチング時間を遅くする可能性がある。カテナンに関する主要な問題は、ON-OFF比が小さいこと、及びスイッチング時間が遅いということである。 50

【0004】

従って、必要とされているのは、化学的酸化及び／又は還元を要さず、第一の状態から第二の状態への適度に速いスイッチングを可能にし、ROM類似デバイスの製造を可能にするほど可逆的であり、且つ種々の電子デバイスに利用できる分子システムである。

【発明の開示】

【発明が解決しようとする課題】

【0005】

本発明によれば、ナノメートルスケールの可逆的な電子スイッチ、詳細には分子配座の変化あるいは異性化を介して生じる電界誘導バンドギャップ変化の起こる電界駆動式分子スイッチ、のための分子システムが提供される。1つの回転部（回転子）と、該回転子とその間に取り付けられている2つの固定部（固定子）とを有する分子システムを提供することによって、バンドギャップを変化させる化学結合変化を介した拡張共役の変化を実現させる。 10

【0006】

本発明は、それを容易に組み合わせることで、クロスバー及びその他の回路を形成することのできるナノメートルスケールの可逆電子スイッチを提供する。クロスバー回路は、上記の一連の特許出願及び発行済み特許において記載されている。当該回路は、記憶装置機能、論理機能、及び通信機能をもたらす。電子スイッチの一例に、所謂、クロスワイヤデバイスがあり、これは、一方のワイヤが0°以外の角度で他方と交差する接合部を形成している一对の交差したワイヤと、前記接合部において前記一对の交差したワイヤを接続させる少なくとも1つのコネクタ種とからなる。前記接合部は、多層の場合にはナノメートル以上の機能寸法を有する。前記コネクタ種は、本明細書において開示且つ特許請求される分子システムからなっている。 20

【発明の効果】

【0007】

本発明は、新しいタイプのスイッチング機構、即ち分子の回転可能な中間部（回転子）の電界誘導回転、を導入する。従って、当該分子はスイッチの切り替えにおいて酸化も還元もされず、よって化学結合を破壊し、不可逆反応を起こす必要性が回避される。また、当該分子の可動部分は極めて小さく、そのため、スイッチング時間が極めて速いものと思われる。また、当該分子は、ロタキサン、及び同族化合物よりも、はるかに単純であり、従ってより容易に且つ安価に製造できる。 30

【0008】

本発明のデバイスは、一般的に、電界デバイスであると考えられ、従って、電気化学的デバイスを扱う初期の実施態様（上述の関連特許出願及び特許に記載されている）とは区別されるべきである。

【0009】

本発明の分子システムは、限定はしないが、記憶装置、論理装置、マルチプレクサ、デマルチプレクサ、集積回路に適合性のあるインターコネクト機器、フィールドプログラマブルゲートアレイ（FPGA）、クロスバースイッチ、及び携帯電話、モバイル機器及びPDAのような通信装置を含む種々の用途において有用性が見出されるものと期待される。 40

【発明を実施するための最良の形態】

【0010】

定義

本明細書で用いられる場合、「接合部」に適用される際の用語「自己整列した」とは、そのどちらかが被覆又は機能化されていてもよい2本のワイヤが互いに交差するところならどこでも、2本のワイヤ間にスイッチ及び／又は他の電氣的接続を形成する接合部が形成されることを意味する。何故なら、接合部を形成するのが交差の働きであるからである。

【0011】

本明細書で用いられる場合、用語「自己組織化」とは、システム構成要素の特性によって、ある種の幾何学的パターンを自然に選択するシステムを意味する。該システムは、その 50

構成を選択することで、そのエネルギーが少なくとも極小となる。

【0012】

用語「一度だけ構成可能な」とは、スイッチが、酸化あるいは還元反応のような不可逆過程を介して一度だけその状態を変えることができることを意味する。そのようなスイッチは、例えば、プログラマブル読出し専用メモリ（PROM）の基礎をなすことができる。

【0013】

用語「再構成可能な」とは、スイッチが、酸化又は還元のような可逆過程を介して多数回その状態を変化させ得ることを意味する。換言すれば、該スイッチは、ランダムアクセスメモリ（RAM）のメモリビットのように、何度も開閉できるものである。

【0014】

分子に適用される際の用語「双安定な」とは、エネルギー（又は活性化）障壁によって隔てられている比較的低い2つのエネルギー状態を有する分子を意味する。該分子は、ある状態から他の状態へ不可逆的に切り替えられるか（一回だけ構成可能）、又はある状態から他の状態に可逆的に切り替えられる（再構成可能）。

【0015】

ミクロンスケールの大きさとは、寸法が1 μm から数 μm に及ぶ大きさを意味する。

【0016】

サブミクロンスケールの大きさとは、0.05 μm から1 μm までの範囲にある大きさを意味する。

【0017】

ナノメートルスケールの大きさとは、0.1 nmから50 nm（0.05 μm ）までの範囲にある大きさを意味する。

【0018】

ミクロンスケール及びサブミクロンスケールのワイヤとは、幅又は直径が0.05 μm から10 μm の大きさであり、高さが数10 nmから1 μm までの範囲にあり、長さが数 μm 以上である棒状又は帯状の導体あるいは半導体を意味する。

【0019】

従来技術のクロスワイヤスイッチに関する基本情報

本質的なデバイスの造作が図1 a－1 bに示されており、また上記関連特許出願及び特許においてより詳しく議論されている。クロスワイヤスイッチ10は、それぞれが0°ではないある角度で交差している金属ワイヤあるいは半導体ワイヤのいずれかである2本のワイヤ12、14からなる。それらのワイヤの間には、図1 a及び1 bにおいてRで示されている分子あるいは分子化合物16の層がある。2本のワイヤ12、14の交差位置で挟まれている特定の分子18（Rsで表示）は、スイッチ分子として取り扱われ、また、本明細書ではその代替用語として接合部とも呼んでいる。そのワイヤの両端に適切な電圧が印加されると、スイッチ分子は、酸化されるかもしくは還元される。分子が酸化（還元）されると、電荷の均衡を保つために、第2の化学種が還元（酸化）される。従って、これらの2つの化学種は、レドックス対と呼ばれる。このデバイスの一例では、1つの分子が還元され、次に第二の分子（レドックス対のもう片方）が酸化される。別の例では、ある分子が還元され、ワイヤの1本が酸化される。第3の例では、ある分子が酸化され、ワイヤの1本が還元される。第4の例では、1つのワイヤが酸化され、もう一方のワイヤと関連付けられている酸化物が還元される。全ての場合において、酸化と還元は、2本のワイヤ間のトンネル距離又はトンネル障壁高さに影響を及ぼし、それによって、ワイヤ接合部を横切る電荷搬送率を指数関数的に変化させ、スイッチの基礎として役立っている。

【0020】

これらのデバイスによって実行される電氣的タスクは、使用されるワイヤ（電極）の種類とワイヤ間物質によって概ね決まる。表1は、図1 a－1 bにおけるワイヤ12、14の種々の組合せから作ることができる種々の種類のデバイスを表している。

【0021】

【表1】

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デバイスの種類	金属- 金属 (同一)	金属- 金属 (異種)	金属- 半導体	半導体- 半導体 (p-n 接合)	半導体- 半導体 (ヘテロ接合)
抵抗体	×	×	×		
トンネル抵抗体	×	×	×		
共鳴トンネル抵抗体	×	×	×		
ダイオード		×	×	×	×
トンネルダイオード		×	×	×	×
共鳴トンネルダイオード		×	×	×	×
バッテリー		×	×		×

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【0022】

ワイヤ（電極）間に使用される分子又は物質に応じて、接合部の各々がワイヤの接点において、すぐ後に述べる種類の電氣的機能を発揮するか、又は接合部は2本のワイヤを電氣的に接続あるいは遮断すべく作用するスイッチ機能を有することができる。該スイッチは、一回だけ構成可能なもの又は再構成可能なもののどちらにもすることができる。第一のケースでは、前記スイッチの初期状態は、開いているか、あるいは閉じている。第二のケースでは、前記スイッチにかけている電圧の極性と振幅を、適切なしきい値を越えて反復させることにより、適切に選択された物質あるいは分子を可逆的に酸化あるいは還元して、そのスイッチを多数回開閉させることが可能である。いずれのケースにおいても、閉じている場合、ワイヤ間で形成される電氣的な接続の種類は、ワイヤ（即ち電極）を構成する材料、並びにワイヤ間の分子あるいは物質の特性に左右される。

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【0023】

前記表1は、電極材料及び接合部に使用される物質あるいは分子の様々な組合せから得ることのできる種々の機能のマトリクス表を示している。抵抗体は、線形の電流－電圧特性を有しており、本質的にワイヤ間で短絡を形成すべく様々な種類のワイヤ間の接合部を意図的に過剰還元することによって作られる。これとは反対の過程は、接合部を過剰酸化することであり、これは局所的な領域でそのワイヤを消費し、接合位置でそのワイヤを効果的に破断する（オープン回路を形成する）。トンネル抵抗体は、ワイヤ間に薄い、約2 nm厚の絶縁障壁を保ち、幾何級数的な電流－電圧特性を有する。接合分子又は物質が、接合部に電氣的にバイアスをかけることでアクセスできる鋭く範囲の限定されたエネルギー状態を電気絶縁障壁のバンドギャップ内に有する場合、ワイヤ間の接続部は、共鳴トンネル過程によって支配される電流の流れを呈することがある。共鳴トンネル効果は、トンネル抵抗体の別の幾何級数的な電流－電圧特性において1つ以上の変曲点を作り出すことができる。ダイオードは、他の方向よりも容易にある方向に電流を流し、従って、正及び負の電圧に関して電流－電圧特性が非対称な接合部である。トンネルダイオードは、ダイオードの正－負電圧の非対称性とトンネル抵抗体の幾何級数的な電流－電圧特性の両方を有する。共鳴トンネルダイオードは、正－負電圧の非対称性を有すると共に、その電流－電圧特性にピークを有しており、それによって、電圧の大きさを増大させていくと、ある限定された範囲において、電流の大きさが実際に減少する、微分負性抵抗として知られている現象を示す。一般に、上述の過程で形成されるワイヤ間の現実の接合部はどれも、有効な回路要素が直列に接続されている状態で、2つ以上の上述の電氣的機能を実際に有することになる。

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【0024】

このように、本発明は、組み立てられた回路が要求するデバイス特性に応じて、任意の数の金属あるいは半導体ワイヤ／分子の組合せによって実施することができる。

【0025】

従来技術のワイヤ電極製造に関する基本的情報
プロセス限定ワイヤ

（従来の電子回路処理技術によって形成されるワイヤとして定義される。ワイヤは、典型

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的に回路の一部として基材上に形成される。)

【0026】

直径が $1\text{ }\mu\text{m}$ から数 μm の範囲（ミクロンスケールとして定義される）、又は直径が 40 nm から $1\text{ }\mu\text{m}$ の範囲（サブミクロンスケールとして定義される）の金属ワイヤ及び半導体ワイヤは、リソグラフィー（光学的、紫外線、又は電子ビーム）技術を含む、よく確立された技術を用いて調製することができる。これらのワイヤは、円形断面を排除するものではないが、通常は帯状又は長方形の断面を有しており、ワイヤの幅は、該ワイヤを画定するのに利用されるリソグラフィープロセスによって決定され、その高さは、リソグラフィーによって画定される領域に付着した材料の量によって定まる。

【0027】

化学的に形成されたワイヤ

（これらのワイヤは、従来の電子的処理技術以外の技術によって形成される。ワイヤは、典型的には、回路板の一部としてよりも、むしろバルク材料として形成される。）

【0028】

金属及び半導体のナノワイヤは、直径が 50 nm 未満（典型的には $2\sim 20\text{ nm}$ ）で、且つ長さが $0.1\text{ }\mu\text{m}\sim 50\text{ }\mu\text{m}$ （典型的には $5\sim 10\text{ }\mu\text{m}$ ）のワイヤとして定義される。これらは、後述の参考文献に記載された多数の技術のうちの任意の1つを使って化学的に製造することができる。

【0029】

半導体元素ゲルマニウムの半導体ナノワイヤを生産する公表済技術の一例は、ゲルマニウム四塩化物とフェニルトリクロロゲルマニウムを、不活性環境下において、密閉容器中 300°C 付近の温度で、数日間、トルエン溶媒中のナトリウム金属の分散物と反応させるものである。本調製によって、直径が $3\sim 30\text{ nm}$ 、且つ長さが $0.5\sim 10\text{ }\mu\text{m}$ の単結晶ゲルマニウムナノワイヤが製造される。

【0030】

半導体元素シリコンの半導体ナノワイヤを生産する公表済技術の第二の例は、シリコン元素及び鉄元素を含有しているターゲットをレーザ蒸発させるものである。ターゲットを 1300°C の真空オーブンに入れて、蒸発処理の間、オーブン中に不活性ガスを流すものである。この技術によって、直径が $20\sim 30\text{ nm}$ の範囲にあり、長さが $1\sim 20\text{ }\mu\text{m}$ の範囲のシリコンワイヤが製造される。

【0031】

金属金元素の金属ナノワイヤを生産する公表済技術の一例は、陽極腐食された酸化アルミニウム薄膜の細孔内部で金のワイヤを電気化学的に成長させるものである。酸化アルミニウムを酸性溶液中で溶かし、金のナノワイヤを解放し、次いで、それを集めるものである。この方法で成長させた金のナノワイヤは、直径が $20\sim 30\text{ nm}$ の範囲にあり、長さが $0.5\sim 5\text{ }\mu\text{m}$ の範囲にある。

【0032】

種々の金属及び半導体物質のナノワイヤが、様々な方法で製造することができる。これらのデバイスの幾つかは、ドーパドSiのようなドーパド半導体ワイヤを必要とするであろう。

【0033】

Siワイヤの場合に関しては、ワイヤを物理的に製造する際に、ワイヤをドーパすることができる。この場合、ワイヤが形成される時に、反応容器中にドーパントを添加することが必要である。例えば、上述のレーザアブレーション／真空オーブンによる製造技術では、例えば三水素化リン（ PH_3 ）あるいは三水素化ヒ素（ AsH_3 ）のような少量のドーパントガスを、レーザアブレーション／ワイヤ形成処理中に、真空オーブン中を流れる不活性ガス（例えば、アルゴン）中に加える。

【0034】

逆に、これらのワイヤは、適切な分子によって、即ち電子求引基（例えば三フッ化ホウ素（ BF_3 ）のようなルイス酸）又は電子供与基（例えばアルキルアミンのようなルイス塩

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基)のどちらかで、それらの表面を被覆することによって変調ドーピングして、それらを、それぞれ、p型又はn型の導体にすることができる。

下記のワイヤ作製手順を参照されたい。図1bは、ワイヤ12上の被覆物20及びワイヤ14上の被覆物22を示す。被覆物20、22には、変調ドーピング被覆物、トンネル障壁(例えば、酸化物)、又はその他のナノスケールの機能的に適切な物質を用いることができる。あるいは又、ワイヤ12、14自体を、1つ以上のR化学種16で被覆することができ、ワイヤが交差する位置にR_s18が形成される。さらにあるいは又、ワイヤ12、14を、例えば、後述するように、一方あるいは両方のワイヤを懸濁させコロイド懸濁液を生成することができる分子種20、22で、それぞれ、被覆することができる。

【0035】

変調ドーピングによってワイヤをドーピングするためには、ワイヤ表面においてSi-O-H基に共有結合する有機あるいは無機分子を用いて、ワイヤ表面を化学的に機能化する必要がある。シリコンナノワイヤは、空気に曝されるとSiO₂の薄い表面層(1nm)が自然に生じ、SiO₂/空気の界面では、SiO₂表面はSi-O-H基で終端している。Si-O-H基に結合するか又はそれを置換する基として、限定はしないが、R-Si(CH₃)_x(OCH₃-_x)、R-Si(CH₃)_x(OCH₂CH₃-_x)、R-Si(CH₃)_xCl_{3-x}、等が挙げられる。この場合、Rは、電子求引基(ルイス酸)あるいは電子供与基(ルイス塩基)を含有することができる有機あるいは無機部分を表している。SiO₂不動態化シリコン表面へ分子を結合させるというこの化学作用は十分確立されているものである。SiO₂不動態化シリコン表面へ分子を結合させるための公表されている1つの例示反応は、下式である。

【0036】

$$\text{Si-O-H}_{(\text{表面})} + \text{R-Si(CH}_3)_2\text{Cl} \rightarrow \text{Si-O-Si(CH}_3)_2\text{R} + \text{HCl}$$

【0037】

その他の半導体ワイヤは、有機アミン、有機チオール、有機リン酸塩等で機能化することができる。

【0038】

明らかなことは、化学的に合成された半導体ワイヤを変調ドーピングする方法についての先の記述は、技術文献には未だ何ら公にされていないことである。

【0039】

例えば金属ナノワイヤのような他のナノワイヤの場合に関しては、ワイヤは、(金ワイヤあるいは銀ワイヤに関しては)R-SHによって、又は(白金ワイヤ及びパラジウムワイヤに関しては)R-NH₂によって、又は(例えばAl₂O₃被覆アルミニウムワイヤあるいはチタンワイヤのような他の金属に関しては)R-CO₂Hによって、化学的に機能化することができ、ここでR基は、例えば当業者が、コロイドのように、溶媒中にワイヤを分散させることができる性質などの、ある化学的性質をワイヤに付与することのできるある有機部分を表している。一実施例において、金ワイヤは、ドデカンチオール(C₁₂H₂₅SH)で機能化することができる。ドデカンチオールは、ワイヤに薄い表面トンネル障壁を設けるのみならず、例えばヘキサンあるいはクロロホルムのような単純な有機溶媒にワイヤを分散させることを可能にする。

【0040】

従来技術のワイヤ作製手順に関する基本情報

下記物質は、列挙された参考文献に従ってナノワイヤとして形成することができる。

シリコン：A. M. Moralesらによる“A laser ablation method for the synthesis of crystalline semiconductor nanowires”、Science、Vol. 279、p. 208-211(1998年1月9日)

ゲルマニウム：J. R. Heathらによる“A liquid solution synthesis of single crystal germanium qu

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antum wires”、Chemical Physics Letters、Vol. 208、pp. 263–268 (1993年6月11日)

金属ナノワイヤ：V. P. Menonらによる“Fabrication and Evaluation of Nano-electrode Ensembles”、Analytical Chemistry、Vol. 67、pp. 1920–1928 (1995年7月1日)

シリコンの機能化：T. Vossmeyerらによる“Combinatorial approaches toward patterning nanocrystals”、Journal of Applied Physics、Vol. 84、pp. 3664–3670 (1998年10月1日) (多数の文献の中の1つ)

金ナノ構造体の表面の機能化：D. V. Leffrらによる“Thermodynamic Size Control of Au Nanocrystals: Experiment and Theory”、The Journal of Physical Chemistry、Vol. 99、p. 7036–7041 (1995年5月4日)

【0041】

重ねて、分子スイッチング構成部分は、デバイスの所望の特性に応じて、多数の様々な種類の分子から作ることができる。その分子に必要な主要な条件は、それらが2つのワイヤ間に挟まれるとき、ワイヤの両端に電圧を印加することにより、それらを電気化学的に変性（即ち、酸化あるいは還元）できるということである。分子構成部分がそのように変性された場合、本質的な効果として、2つのワイヤ間のトンネル障壁が変化し、電流の流れる比率が変化する。これは、次には、記憶装置、論理演算、及び通信及び信号ルーティングネットワークに利用できるスイッチの基礎をなす。分子スイッチは、分子のレドックス対を含むことができ、この場合、電圧の印加によって、分子の1つが還元され、他が酸化される。そのような分子のレドックス対の例として、テトラブチルアンモニウムヘキサフルオロリン酸塩 (Bu_4NPF_6) に対するニッケロセン（ジシクロペンタジエニル ニッケル）、即ち Cp_2Ni が挙げられる。その場合には、その反応は下式のようになる。

【0042】

(還元) $\text{Cp}_2\text{Ni} + \text{Bu}_4\text{NPF}_6 \rightarrow \text{Cp}_2\text{Ni}^- + \text{Bu}_4\text{NPF}_6^+ \quad (-1.7\text{V})$

又は、

(酸化) $\text{Cp}_2\text{Ni} + \text{Bu}_4\text{NPF}_6 \rightarrow \text{Cp}_2\text{Ni}^+ + \text{Bu}_4\text{NPF}_6^- \quad (-0.1\text{V})$

【0043】

ニッケロセン系は、溶液相サイクリックボルタンメトリーによって測定されるように、その還元が極めて非対称であるという点において特に興味深い。そのような非対称性は、安定で且つ書き換え可能な磁気記憶装置の基礎をなす磁化履歴曲線に相似している。しかし、酸素の存在下では、ニッケロセンの還元は、溶液相サイクリックボルタンメトリーで測定されるように、不可逆である。いずれの場合でも、この系の還元あるいは酸化は、分子がその間に挟まれる2本のワイヤ間のトンネル障壁を変化させる。従って、この系は、再構成可能なもの、又は一回だけ構成可能なもののどちらかのタイプの分子スイッチとして機能することができる。メタロセン系に関しては、例えば、J. D. L. Hollowayらによる“Electron-transfer reactions of metallocenes: Influence of metal oxidation state on structure and reactivity”、Journal of the American Chemical Society、Vol. 101、pp. 2038–2044 (1979年4月11日)を参照されたい。

【0044】

コネクタ種16は、溶液の電気化学作用もしくは固体状態の接合部における電流－電圧特性のいずれかから得られた、電流－電圧曲線において顕著な、即ち測定可能なヒステリシスを示す物質からなる。そのような種の例として、メタロセン、ロタキサン、疑似ロタキサン、及びカテナンが挙げられ、それらは分子内水素結合に依存している。しかしながら、そのような分子は開示された目的にとって有用であるが、単純な分子内水素結合力は、

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上述のように、ある条件下では、比較的容易に越えられる。

【0045】

本発明

本発明によって、分子は、外部電界によって切り替え得る能動電子スイッチとなる。共通する概念は、大きい双極子モーメントを有し（例1及び2参照）且つ固定化されている分子の他の2つの部分（固定子）を連結する回転可能な中間部分（回転子）を分子中に設計することである。印加電界の影響下、回転子のベクトル双極子モーメントは、外部電界の方向に平行に配列しようとする。しかしながら、分子は、回転子を固定子に関して特定の方位で安定化させる、例えば水素結合、双極子-双極子相互作用並びに立体斥力のような分子間及び／又は分子内力が存在するように設計されている。従って、もし印加電界が回転子の双極子の方向と逆である場合、回転子をその最初の方位から外して固定子に関して回転させるには、大きい電界を必要とする。特定方位にいったん切り替えられると、分子は、切り替えられるまでその方位に留まる。しかしながら、分子設計の重要な要素は、回転子が完全に180°反転するまで回転するのを妨ぐことのできる立体斥力があることである。代わりに、その回転は、回転子及び固定子上の大きな基の立体相互作用によって、最初の方位からほぼ90°の角度で止められる。さらに、この90°方位は、異なった組の分子間及び／又は分子内水素結合あるいは双極子相互作用によって安定化され、従って、印加電界が解除された後でも定位置に留まる。スイッチ分子には、固定子からほぼ90°だけ隔てられた2つの状態の間に回転子を留めるこの能力は重要である。

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【0046】

理想的には、回転子及び固定子が、全て、同一面上にあるとき、その分子は、完全に共役されている。従って、p、 π 電子は、その最高被占分子軌道（HOMO）及び最低空分子軌道（LUMO）を介して、分子全体にわたって非局在化している。これは、分子の高導電（スイッチON）状態である。回転子が固定子に関して90°だけ回転している場合、分子の共役が破壊され、HOMO及びLUMOは、もはや分子全体にわたって非局在化していない。これは、分子の低導電（スイッチOFF）状態である。こうして、分子は、ON及びOFF状態の間で可逆的に切り替えることができる。

【0047】

この固定子-回転子-固定子モデルでは、以下の要件が満たされなければならない。

【0048】

(a) 分子は、1つの回転子部と2つの固定子部とを有していなければならない。

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【0049】

(b) 分子のある状態では、分子全体（回転子及び固定子）の大部分にわたって拡張する非局在化HOMO及び／又はLUMO（ π 状態及び／又は非結合軌道）が存在し、その他の状態では、その軌道が回転子及び固定子上に局在化している。

【0050】

(c) 回転子と各固定子間の接続ユニットには、(1) 非結合電子（pあるいは他の電子）、あるいは(2) π 電子、あるいは(3) π 電子及び非結合電子（単数又は複数）、を有する1つの σ 結合あるいは少なくとも1つの原子とすることができる。

【0051】

(d) 電界による活性化時に回転子が回転する間、回転子及び固定子の非結合電子、あるいは π 電子、あるいは π 電子及び非結合電子（単数又は複数）を、分子の配座に応じて、局在化あるいは非局在化させることができる。

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【0052】

(e) 分子の配座（単数又は複数）は、電界依存性あるいは双安定性とすることができる。

【0053】

(f) 双安定状態（単数又は複数）は、例えば水素結合、クーロン力、ファンデルワールス力、金属イオン錯体相互安定化あるいは双極子相互安定化のような分子内あるいは分子間力によって達成することができる。

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【0054】

(g) 分子のバンドギャップは、非結合電子、あるいは π 電子、あるいは π 電子及び非結合電子（単数又は複数）の非局在化の程度に応じて変化する。これによって、分子の導電率のような電気的特性が変化する。

【0055】

以下は、本モデルの2つの例（例1及び2）である。

【0056】

本発明の新規の2モード分子は、外部電界によって切り替え可能な能動電子デバイスである。その全般的な概念は、図2に示すように、大きい双極子モーメントを有し（例1及び2参照）且つ固定化されている分子30の他の2つの部分（固定子）34を連結する回転可能な中間部分（回転子）32を分子中に設計することである。印加電界の影響下、回転子32のベクトル双極子モーメントは、外部電界の方向に平行に配列しようとする。しかしながら、分子30は、回転子32を固定子34に関して特定の方位で安定化させる、例えば水素結合、双極子-双極子相互作用並びに立体斥力のような分子間及び／又は分子内力が存在するように設計されている。従って、回転子32をその最初の方位から外して固定子34に関して回転させるには、大きい電界を必要とする。

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【0057】

特定方位にいったん切り替えられると、分子30は、異なる方位に切り替えられるまで、あるいは構成変更されるまで、その方位に留まるしかしながら、分子設計の重要な要素は、回転子32が完全に180°反転するまで回転するのを妨ぐことのできる立体斥力があることである。代わりに、その回転は、回転子32及び固定子34上の大きな基の立体相互作用によって、初期の方位から通常10°～170°の電氣的に有効な角度で止められる。例示のために、この角度は、本出願では90°として示す。さらに、この切替えの方位は、異なった組の分子間及び／又は分子内水素結合あるいは双極子相互作用によって安定化され、従って、印加場が解除された後でも定位置に留まる。双安定スイッチ分子の場合、固定子から電氣的に有効な角度だけ隔てられた2つの状態間に回転子32を留めるこの能力は、極めて重要である。

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【0058】

回転子32及び固定子34が全て同一平面上にあるとき、その分子は「共役が強い」と呼ばれる。従って、分子の非結合電子、あるいは π 電子、あるいは π 電子及び非結合電子は、その最高被占分子軌道（HOMO）及び最低空分子軌道（LUMO）を介して、分子30の大部分にわたって非局在化している。これを、当該分子の「高導電状態」、あるいは「電氣的状態I」と呼ぶ。回転子32が固定子34に関して約10°～170°だけ共役から回転している場合には、分子30の共役が破壊され、HOMO及びLUMOは分子のより小さな部分にわたって局在化し、「共役が弱い」と呼ばれる。これは、分子30の「低導電状態」、あるいは「電氣的状態II」である。従って、分子30は、2つの異なる電氣的状態間で可逆的に切り替わることができる。

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【0059】

理想的な場合には、回転子32及び固定子34が完全に同一平面上にあるときには、分子は完全に共役しており、回転子32が固定子34に関して90°の角度に回転しているときには、分子は共役していないことが、当業者には理解されよう。しかしながら、熱によるゆらぎに起因して、これらの理想的な状態は完全には実現されず、それゆえ分子は、前者の場合には「共役が強い」と呼ばれ、後者の場合には「共役が弱い」と呼ばれる。

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【0060】

例1及び2は、分子を切り替えるための2つの異なる方位を示す。例1において、回転子の回転軸は、分子の実質的な電流搬送軸にほぼ垂直になるよう設計されているが、例2では、その回転軸は、分子の方位軸に平行になっている。これらの設計によって、所望する結果に応じて、異なる形状の分子薄膜及び電極を用いることができる。一般的な分子構造及び実際の分子構造の両方を、例毎に示す。例1a及び例2aは、分子を切り替えるための2つの異なる方位を示している一般的な分子構造であり、例1b及び例2bは2つの実

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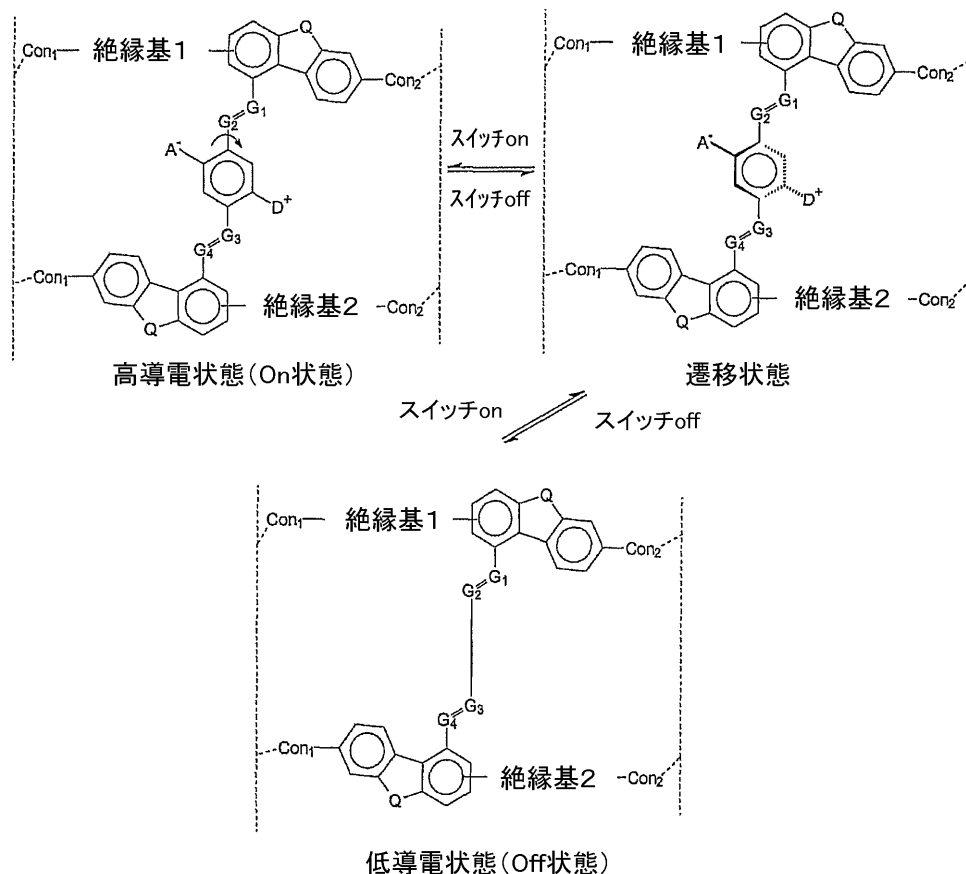
際の分子構造である。

【0061】

最初に例1を参照すると、本発明の双安定分子メカニカルデバイスの第1の実施形態が示されている。以下の例1aは、固定子—回転子—固定子モデルに関する一般的な分子の実施形態を示す。

【0062】

【化5】



例 1a

【0063】

ここで、文字 A^- は、受容体基を表し、それは電子求引基である。それは、水素、カルボン酸あるいはその誘導体、硫酸あるいはその誘導体、リン酸あるいはその誘導体、ニトロ、ニトリル、ヘテロ原子（例えば、N、O、S、P、F、Cl、Br）、あるいは前記ヘテロ原子のうちの少なくとも1つを有する官能基（例えば、OH、SH、NH等）、炭化水素（飽和あるいは不飽和のいずれか）あるいは置換炭化水素、のうちの1つとすることができる。

【0064】

文字 D^+ は、供与体基を表し、それは電子供与基である。それは、水素、アミン、OH、SH、エーテル、炭化水素（飽和あるいは不飽和のいずれか）、あるいは置換炭化水素、あるいは少なくとも1つのヘテロ原子（例えば、B、Si、N、O、S、P、I）を有する官能基、のうちのいずれか1つとすることができる。供与体は、当該分子上の受容体基よりも電氣的陰性が低いか、あるいは電氣的陽性が高いという事実によって受容体とは区別される。

【0065】

文字 Con_1 及び Con_2 は、ある分子と固体基材（例えば、金属電極、無機あるいは有機基材等）との間の接続ユニットを表す。それらは、水素（水素結合を利用する）、多価

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ヘテロ原子（即ち、C、N、O、S、P等）、あるいはこれらのヘテロ原子を含む官能基（例えば、NH、PH等）、炭化水素（飽和あるいは不飽和のいずれか）、あるいは置換炭化水素、のうちの任意のものとすることができる。

【0066】

文字 G_1 、 G_2 、 G_3 及び G_4 は、ブリッジング基である。これらブリッジング基の機能は、所望の電子特性を得るために、固定子と回転子とを接続するか、又は2つ以上の共役環を接続することである。それらは、ヘテロ原子（例えば、N、O、S、P等）、あるいは上記ヘテロ原子のうちの少なくとも1つを有する官能基（例えば、NHあるいはNHNH等）、炭化水素（飽和あるいは不飽和のいずれか）、あるいは置換炭化水素、のうちの任意のものとすることができる。あるいは又、該コネクタは、酸素原子によるエーテルブリッジのような単原子ブリッジ、又は回転子と固定子との間の直接シグマ結合により構成

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【0067】

本明細書では、文字Qは、2つのフェニル環間の接続ユニットを示すために用いられる。それは、S、O、NH、NR、炭化水素あるいは置換炭化水素、のうちの任意のものとすることができる。

【0068】

上記の例1aにおいて、垂直方向の点線は、他の分子あるいは固体基材を表す。スイッチング電界の向きは、前記垂直方向の点線に対して垂直である。そのような構成は、電気的なスイッチングのために用いられ、その分子は単に2つの電極間に配置することができる

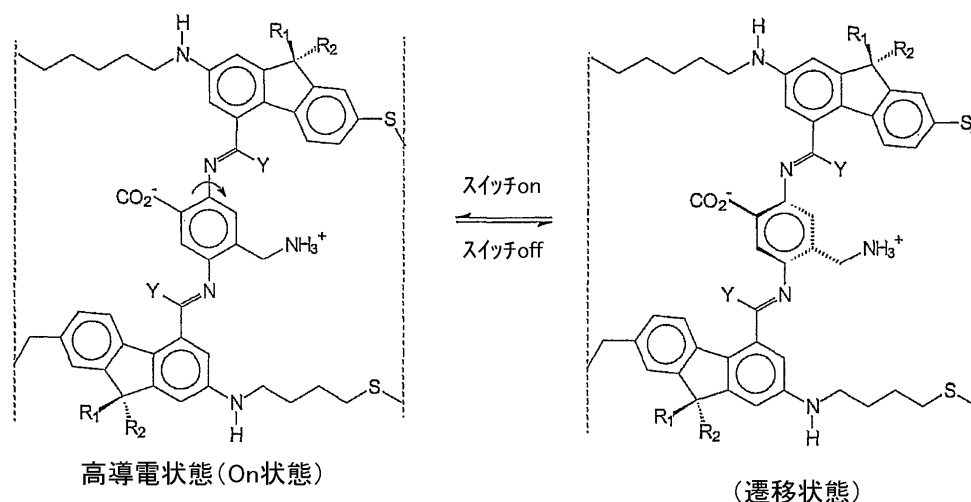
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【0069】

以下の例1bは、前記固定子－回転子－固定子モデルの実際の分子の例である。

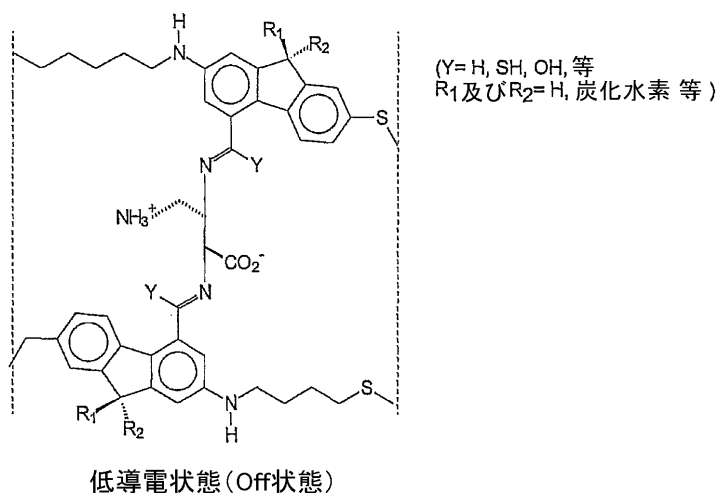
【0070】

【化6】



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スイッチon
スイッチoff



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例 1b

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【0071】

上記の分子（例1b）は、内部回転子32が分子30全体の方位軸に対して垂直になるように設計されている。この場合、外部電界は図示するように分子30の方位軸に沿って印加され、電極（垂直方向の点線）は紙面に対して垂直に、且つ分子30の方位軸に対して垂直に向けられる。図面の左から右に配向された電界の印加によって、左上の図面に描かれたような回転子32を下の図面に示す位置まで回転させることができ、またその逆も可能である。この場合、下の図面に描かれたような回転子32は、分子の他の部分と同一平面上になく、そのため、これは分子のOFF、即ち低導電状態であり、一方、左上の図面では回転子が分子の他の部分と実質的に同一平面上にあるので、これは分子のON、即ち高導電状態である。右上の図面に示す構造は、左上の図面（同一平面、共役）と下の図面（中央部が回転、非共役）との間の回転の移行の様子を表している。

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【0072】

例1に示す分子は、非共役状態において非導電性（あるいは比較的低導電性）である。共役状態では、当該分子は導電性である。

【0073】

例1に示す種類の分子の場合、例えばラングミュアブロッジェット法あるいは自己組織化単層を用いて、単一の単層分子膜を成長させて、それによって、分子の方位軸が、分子を切り替えるのに用いられる電極面に垂直になるようにする。電極は、上記のCollierらに

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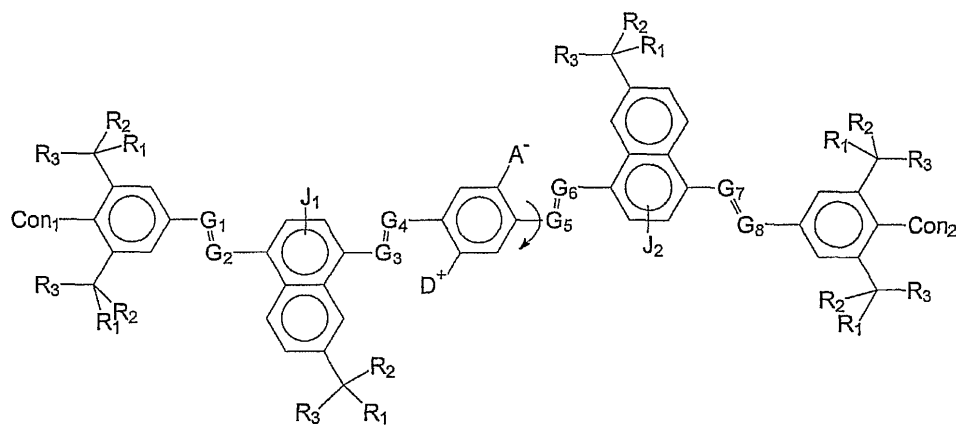
よって示された方法で、又は前述の特許出願及び発行済特許に記載されている方法で、付着させることができる。

【0074】

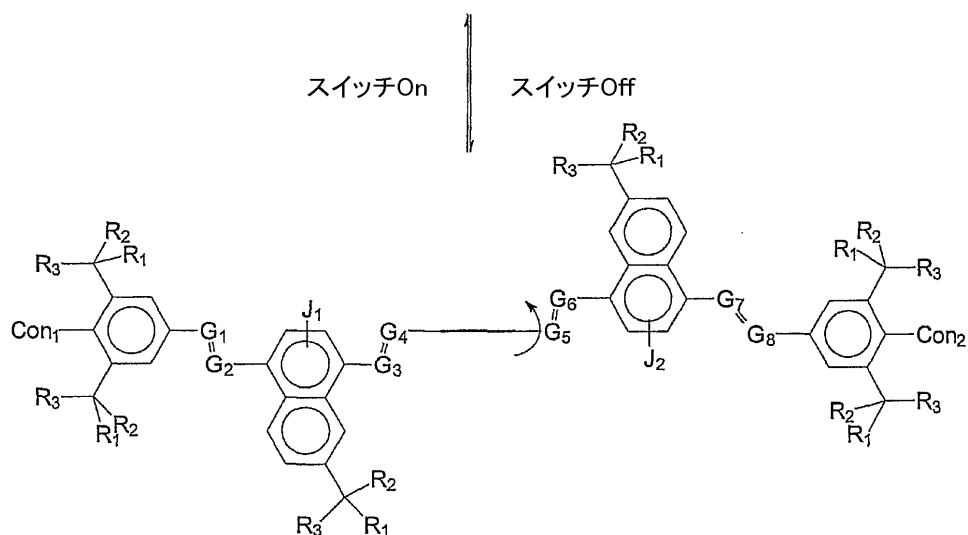
次に例2を参照すると、本発明の双安定分子メカニカルデバイスの第2の実施形態が示されている。以下の例2aは、本発明の固定子一回転子固定子形態に関する第2の一般的な分子の例を示している。

【0075】

【化7】



On状態(高導電状態)



Off 状態(低導電状態)

例 2a

【0076】

ここで、文字 A^- は、受容体基を表し、それは電子求引基である。それは、水素、カルボン酸あるいはその誘導体、硫酸あるいはその誘導体、リン酸あるいはその誘導体、ニトロ、ニトリル、ヘテロ原子（例えば、N、O、S、P、F、Cl、Br）、あるいは前記ヘテロ原子のうちの少なくとも1つを有する官能基（例えば、OH、SH、NH等）、炭化水素（飽和あるいは不飽和のいずれか）、あるいは置換炭化水素、のうちの1つとすることができる。

【0077】

文字 D^+ は、供与体基を表し、それは電子供与基である。それは、水素、アミン、OH、

S H、エーテル、炭化水素（飽和あるいは不飽和のいずれか）、あるいは置換炭化水素、あるいは少なくとも1つのヘテロ原子（例えば、B、S i、I、N、O、S、P）を有する官能基、のうちのいずれか1つとすることができる。供与体は、当該分子上の受容体基よりも電氣的陰性が低いか、あるいは電氣的陽性が高いという事実によって受容体とは区別される。

【0078】

文字C o n₁ 及びC o n₂ は、ある分子と他の分子との間の、又はある分子と固体基材（例えば、金属電極、無機あるいは有機基材等）との間の接続ユニットを表す。それらは、水素（水素結合を利用する）、多価ヘテロ原子（即ち、C、N、O、S、P等）、あるいはこれらヘテロ原子を含む官能基（例えば、NH、PH等）、炭化水素（飽和あるいは不飽和のいずれか）、あるいは置換炭化水素、のうちの任意のものとする事ができる。

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【0079】

文字R₁、R₂ 及びR₃ は、分子に組み込まれているスペーシング基を表す。これらのスペーシングユニットの機能は、各回転子のための回転の空間を設けながら、分子が密集できるようにするための適切な3次元の枠組みを設けることである。それらは、水素、炭化水素（飽和あるいは不飽和のいずれか）、あるいは置換炭化水素、のうちの任意のものとする事ができる。

【0080】

文字G₁、G₂、G₃、G₄、G₅、G₆、G₇ 及びG₈ は、ブリッジング基を表す。これらのブリッジング基の機能は、所望の電子特性を得るために、固定子と回転子とを接続するか、又は2つ以上の共役環を接続することである。それらは、ヘテロ原子（例えば、C、N、O、S、P等）、あるいは前記ヘテロ原子のうちの少なくとも1つを有する官能基（例えば、NHあるいはNHNH等）、炭化水素（飽和あるいは不飽和のいずれか）、あるいは置換炭化水素、のうちの任意のものとする事ができる。あるいは又、該コネクタは、酸素原子によるエーテルブリッジのような単原子ブリッジ、又は回転子と固定子との間の直接シグマ結合から構成することができる。

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【0081】

文字J₁ 及びJ₂ は分子に組み込まれている調整基を表す。これらの調整基（例えば、OH、NHR、COOH、CN、ニトロ等）の機能は、適切な機能的効果（例えば、誘導性効果及び共鳴効果の両方）及び／又は立体効果をもたらすことである。機能的効果とは、分子のバンドギャップ（ $\Delta E_{HOMO/LUMO}$ ）を調整し、分子の所望の電子的特性を得ることである。立体効果とは、立体障害、分子間あるいは分子内相互作用力（例えば、水素結合、クーロン相互作用、ファンデルワールス力）を介して分子配座を調整することや、あるいは分子の方位の双安定性あるいは多重安定性をもたらすことである。それらは、水素、ヘテロ原子（例えば、N、O、S、P、B、F、Cl、Br及びI）、前記ヘテロ原子のうちの少なくとも1つを有する官能基、炭化水素（飽和あるいは不飽和のいずれか）あるいは置換炭化水素、のうちの任意のものとする事ができる。

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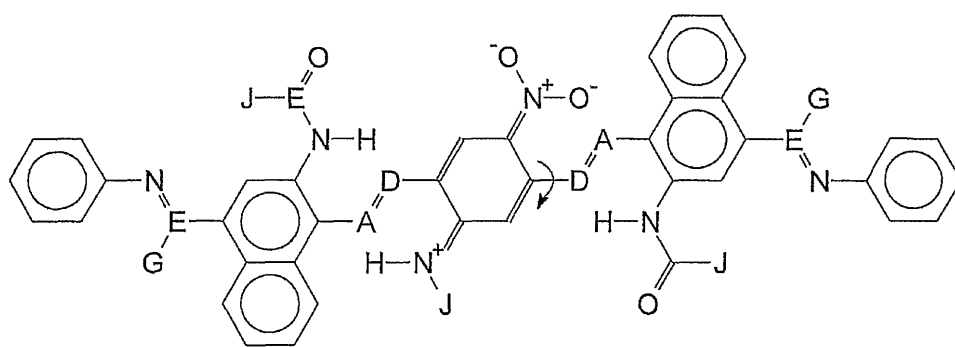
【0082】

以下の例2 bは、前記固定子－回転子－固定子形態の、実際の分子の一例である。

【0083】

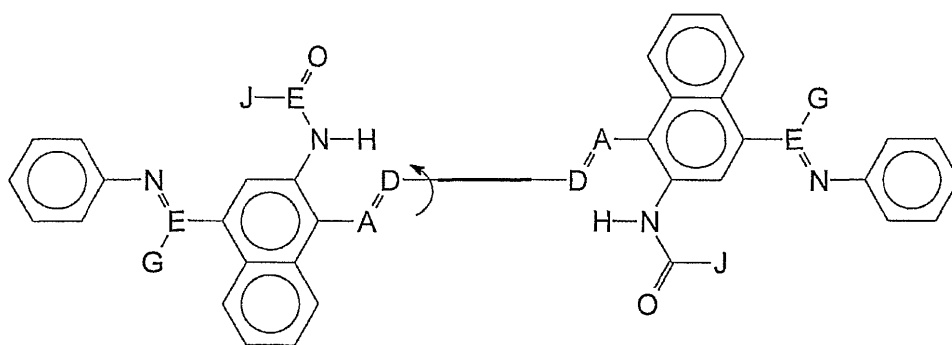
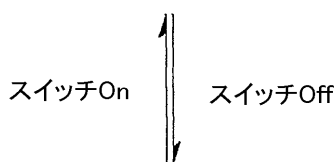
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【化8】



高導電状態(On状態)

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低導電状態(Off 状態)

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例 2b

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【0084】

上記分子（例2b）は、分子全体の方位軸に平行な内部回転子を用いて設計されている。この場合、外部電界は、分子軸に垂直に印加される。電極は、分子の長軸に平行に配向され、且つ上記モデル構造の面に垂直か又は平行に配向させることができる。例えば、電界線が分子軸に対して垂直で且つ上方を指している電界を上記上側分子へ印加することによって、その図に描かれている回転子は、上記下側分子図面に示すように、ほぼ90°回転し、エッジが現出する。この逆も可能である。この場合、下側図面に描かれたような回転子は、分子の他の部分と同一面上になく、そのため、これは分子のOFF、即ち低導電状態であり、一方、上側図面では、回転子が分子の他の部分と同一面上にあり、そのため、これは分子のON、即ち高導電状態である。同図面において、文字A、D、E、G、及びJは、分子の幾何構造を調節するのに種々の化学ユニットを利用でき、且つ他の化学特性基も回転子及び固定子として使用することができる部位を表している（文字N、H、及びOは、それらの通常の意味を保持している）。文字A、D、E、G及びJは、ヘテロ原子（例えば、N、O、S、P等）、炭化水素（飽和あるいは不飽和のいずれか）、あるいは前記ヘテロ原子のうちの少なくとも1つを有する炭化水素、のうちの任意のものとする事ができる。上記の内容に加えて、文字G及びJは、水素、F、Cl、Br、I等のヘテロ原子のうちの任意のものとする事ができる。

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【0085】

例2の分子に関しては、分子軸が電極面に対して平行になるように薄膜を成長させる。こ

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れによって、多数の単層が重なり合った膜が生じる。分子は、固体状態あるいは液晶を形成し、大きい固定子基は分子間相互作用あるいは支持構造への直接結合によって所定の位置に固定されるが、回転子は分子の格子内部で動けるほど十分に小さい。電極を適切に配置することで、この構造は、ゲート接合（トランジスタ）、即ち、1つの電極に印加された電圧が、分子によって架橋されている2つの他の電極間に流れる電流を制御するもの、を作り出すのに用いることができる。

【0086】

例2 a及び例2 bでは接続ユニットを示していないが、例えば例1 a及び1 bに示した一Sーのような接続ユニットを用いて、例1で描いたような一对の電極間に分子を接続することができる。詳細には、分子の固定子部と電極との間を接続する。

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【0087】

例1及び2は、分子を切り替えるための2つの異なる方位を示す。しかしながら、示した例は、本発明を、図示した特定の分子システムに限定することを意図したものではなく、本明細書に開示し、特許請求するスイッチング機構を単に例示するものにすぎない。

【0088】

従って、本発明は従来技術とは明らかに異なる新しい種類のスイッチング機構、即ち分子のバンドギャップを変化させる分子の回転可能部位（回転子）の電界（E界）誘導回転、を導入する。従来技術の手法とは対照的に、スイッチを切り替える際に、分子は酸化も還元もされない。また、分子の可動部は極めて小さいので、スイッチング時間が非常に速いものと期待される。また、その分子は、ロタキサン、カテナン及び同族化合物よりもはるかに単純であり、それゆえ容易且つ安価に製造することができる。

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【0089】

本明細書において開示し、且つ特許請求したクロスワイヤ（ μm 又は nm ）を形成するための技術は、種々の機能を実行するのに利用することができ、且つ計算を実施するための種々の有用なデバイスをミクロンスケールでさらにはナノスケールで形成するのに利用することができる。例えば、用途として、信号ルートの選択及び通信用の分子ワイヤクロスパーインターコネクト機器（MWCI）、分子ワイヤクロスパー記憶装置（米国特許第6、128、214号）、プログラマブル論理アレイを採用した分子ワイヤクロスパーロジック（MWCL）、分子ワイヤクロスパーネットワーク用のデマルチプレクサ、分子ワイヤトランジスタ、及び表示用ピクセルアレイが挙げられる。

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【0090】

図3に示すように、本発明のスイッチ10は、クロスパースイッチを形成するために、多数のスイッチ、即ちスイッチアレイ60を形成できるように二次元の配列に反復させることができる。図3では 6×6 アレイ60を示しているが、本発明は、アレイ内において、特定の数の要素、即ちスイッチに限定されるものではない。ある個々の点、例えば2 bへのアクセスは、上述のように、ワイヤ2及びbに電圧を印加し、その接合部において分子種18の状態変化を起こすことによりなされる。こうして、各接合部へアクセスすることで、本明細書の教示に従って、予め選択された接合部のみを構成することができる。クロスパースイッチアレイ60の動作の詳細は、上記米国特許第6、128、214号にさらに詳しく論じられている。

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【産業上の利用可能性】

【0091】

本明細書に開示する電界により切り替え可能な分子は、マイクロスケール及びナノスケールの電子デバイスにおいて用途が見出されるものと期待される。

【図面の簡単な説明】

【0092】

【図1 a】2本のワイヤの交点に少なくとも1つの分子を有する2つの交差したワイヤの概略図

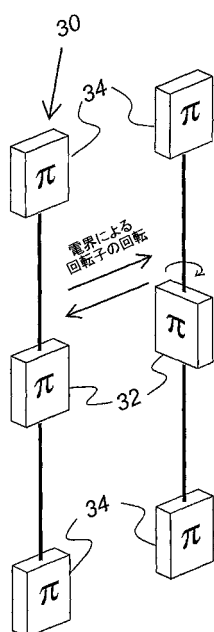
【図1 b】図1 a記載のデバイスを示す斜視正面図

【図2】分子配座の変化を介する電界誘導バンドギャップ変化を表す概略モデル（回転子

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【図 3】 6×6 クロスバースイッチを示す本発明のスイッチの二次元配列を示す概略図

【图 2】



【国際公開パンフレット】

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

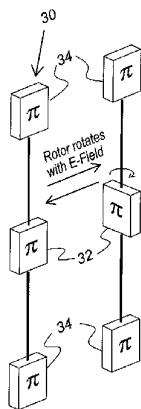
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(54) Title: BISTABLE MOLECULAR MECHANICAL DEVICES WITH A MIDDLE ROTATING SEGMENT ACTIVATED BY AN ELECTRIC FIELD FOR ELECTRONIC SWITCHING, GATING, AND MEMORY APPLICATIONS



(57) Abstract: A molecular system (30) is provided for electric field activated switches, such as a crossed-wire device (10) or a pair of electrodes (12, 14) to which the molecular system (30) is linked by linking moieties. The cross-wire device (10) comprises a pair of crossed wires (12, 14) that form a junction (18) where one wire (14) crosses another (12) at an angle other than zero degrees and at least one connector species (16) connecting the pair of crossed wires (12, 14) in the junction (18). The connector species (16) comprises the molecular system (30), which has an electric field induced band gap change, and thus a change in its electrical conductivity, that occurs via one a molecular conformation change, based on a rotor/stator construction of the molecular system (30), involving a rotating portion (rotor) (32) connected between the stationary portions (stators) (34). Nanometer-scale reversible electronic switches (10) are thus provided that can be assembled easily to make cross-bar circuits (60), which provide memory, logic, and communication functions.

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10 BISTABLE MOLECULAR MECHANICAL DEVICES WITH A
MIDDLE ROTATING SEGMENT ACTIVATED BY AN ELECTRIC
FIELD FOR ELECTRONIC SWITCHING, GATING, AND
MEMORY APPLICATIONS

15 TECHNICAL FIELD

The present invention relates generally to electronic devices whose functional length scales are measured in nanometers, and, more particularly, to classes of molecules that provide electronic switching. Electronic devices both of micrometer and nanometer scale may be constructed in accordance with the teachings herein.

20

BACKGROUND ART

The area of molecular electronics is in its infancy. To date, there have been two convincing demonstrations of molecules as electronic switches published in the technical literature; see, C.P. Collier et al., Science, Vol. 285, pp. 391-394 (16 July 1999) and C.P. Collier et al., Science, Vol. 289, pp. 1172-1175 (18 August 2000), but there is a great deal of speculation and interest within the scientific community surrounding this topic. In the published work, a molecule called a rotaxane or a catenane was trapped between two metal electrodes and caused to switch from an ON state to an OFF state by the application of a positive bias across the molecule. The ON and OFF states differed in resistivity by about a factor of 100 and 5, respectively, for the rotaxane and catenane.

The primary problem with the rotaxane was that it is an irreversible switch. It can only be toggled once. Thus, it can be used in a programmable read-only memory (PROM), but not in a ROM-like device nor in a reconfigurable system, such as a defect-tolerant communications and logic network. In addition, the rotaxane requires an oxidation and/or reduction reaction to occur

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before the switch can be toggled. This requires the expenditure of a significant amount of energy to toggle the switch. In addition, the large and complex nature of rotaxanes and related compounds potentially makes the switching times of the molecules slow. The primary problems with the catenanes are small ON-to-OFF ratio and a slow switching time.

5 Thus, what is needed is a molecular system that avoids chemical oxidation and/or reduction, permits reasonably rapid switching from a first state to a second, is reversible to permit the fabrication of ROM-like devices, and can be used in a variety of electronic devices.

DISCLOSURE OF INVENTION

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In accordance with the present invention, a molecular system is provided for nanometer-scale reversible electronic switches, specifically, electric field activated molecular switches that have an electric field induced band gap change that occurs via a molecular conformation change or an isomerization. Changing of extended conjugation via chemical bonding change to change the band gap is accomplished by providing the molecular system with one rotating portion (rotor) and two stationary portions (stators), between which the rotor is attached.

15

The present invention provides nanometer-scale reversible electronic switches that can be assembled easily to make cross-bar and other circuits. The cross-bar circuits have been described in the above-listed series of patent applications and issued patent. The circuits provide memory, logic and communications functions. One example of the electronic switches is the so-called crossed-wire device, which comprises a pair of crossed wires that form a junction where one wire crosses another at an angle other than zero degrees and at least one connector species connecting the pair of crossed wires in the junction. The junction has a functional dimension in nanometers or larger for multilayers. The connector species comprises the molecular system disclosed and claimed herein.

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The present invention introduces a new type of switching mechanism, namely, an electric field induced rotation of a rotatable middle section (rotor) of a molecule. Thus, the molecule is neither oxidized nor reduced in the toggling of the switch, which avoids the necessity of breaking chemical bonds and potentially initiating a nonreversible reaction. Also, the part of the molecule that moves is quite small, so the switching time should be very fast. Also, the molecules are much simpler and thus easier and cheaper to make than the rotaxanes and related compounds.

30

The devices of the present invention are generically considered to be electric field devices, and are to be distinguished from earlier embodiments (described in the above-mentioned related patent applications and patent) that are directed to electrochemical devices.

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The molecular system of the present invention is expected to find use in a variety of applications, including, but not limited to, memories, logic devices, multiplexers, demultiplexers,

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configurable interconnects for integrated circuits, field-programmable gate arrays (FPGAs), cross-bar switches, and communication devices, such as cellular phones, mobile appliances, and PDAs.

BRIEF DESCRIPTION OF THE DRAWINGS

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FIG. 1a is a schematic representation of two crossed wires, with at least one molecule at the intersection of the two wires;

FIG. 1b is a perspective elevational view, depicting the device shown in FIG. 1a;

FIG. 2 is a schematic model depicting an E-field-induced band gap change via molecular conformation change (rotor/stator type of model); and

FIG. 3 is a schematic representation of a two-dimensional array of switches of the present invention, depicting a 6x6 crossbar switch.

BEST MODES FOR CARRYING OUT THE INVENTION

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Definitions

As used herein, the term "self-aligned" as applied to "junction" means that the junction that forms the switch and/or other electrical connection between two wires is created wherever two wires, either of which may be coated or functionalized, cross each other, because it is the act of crossing that creates the junction.

The term "self-assembled" as used herein refers to a system that naturally adopts some geometric pattern because of the identity of the components of the system; the system achieves at least a local minimum in its energy by adopting this configuration.

The term "singly configurable" means that a switch can change its state only once via an irreversible process such as an oxidation or reduction reaction; such a switch can be the basis of a programmable read-only memory (PROM), for example.

The term "reconfigurable" means that a switch can change its state multiple times via a reversible process such as an oxidation or reduction; in other words, the switch can be opened and closed multiple times, such as the memory bits in a random access memory (RAM).

The term "bi-stable" as applied to a molecule means a molecule having two relatively low energy states separated by an energy (or activation) barrier. The molecule may be either irreversibly switched from one state to the other (singly configurable) or reversibly switched from one state to the other (reconfigurable).

Micron-scale dimensions refers to dimensions that range from 1 micrometer to a few micrometers in size.

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Sub-micron scale dimensions refers to dimensions that range from 1 micrometer down to 0.05 micrometers.

Nanometer scale dimensions refers to dimensions that range from 0.1 nanometers to 50 nanometers (0.05 micrometers).

5 Micron-scale and submicron-scale wires refers to rod or ribbon-shaped conductors or semiconductors with widths or diameters having the dimensions of 0.05 to 10 micrometers, heights that can range from a few tens of nanometers to a micrometer, and lengths of several micrometers and longer.

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Basic Information on Prior Art Crossed Wire Switches

The essential device features are shown in FIGS. 1a-1b and are discussed in greater detail in the above-related patent applications and patent. A crossed wire switch 10 comprises two wires 12, 14, each either a metal or semiconductor wire, that are crossed at some non-zero angle. In between those wires is a layer of molecules or molecular compounds 16, denoted R in FIGS. 1a and 1b. The particular molecules 18 (denoted R_n) that are sandwiched at the intersection of the two wires 12, 14 are identified as switch molecules, also interchangeable referred to herein as a junction. When an appropriate voltage is applied across the wires, the switch molecules are either oxidized or reduced. When a molecule is oxidized (reduced), then a second species is reduced (oxidized) so that charge is balanced. These two species are then called a redox pair. One example of this device would be for one molecule to be reduced, and then a second molecule (the other half of the redox pair) is oxidized. In another example, a molecule is reduced, and one of the wires is oxidized. In a third example, a molecule is oxidized, and one of the wires is reduced. In a fourth example, one wire is oxidized, and an oxide associated with the other wire is reduced. In all cases, oxidation or reduction will affect the tunneling distance or the tunneling barrier height between the two wires, thereby exponentially altering the rate of charge transport across the wire junction, and serving as the basis for a switch.

20 The electrical tasks performed by these devices are largely determined by the types of wires (electrodes) and the interwire materials that are used. Table I presents the various types of devices that might be fabricated from various combinations of the wires 12, 14 in FIGS 1a-1b.

Table I. Wire (Electrode) Materials

Device Type	Metal-metal (same)	Metal-metal (different)	Metal-semiconductor	Semiconductor-Semiconductor (p-n junction)	Semiconductor-semiconductor (heterojunction)
Resistor	X	X	X		

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Tunneling resistor	X	X	X		
Resonant tunneling resistor	X	X	X		
Diode		X	X	X	X
Tunneling diode		X	X	X	X
Resonant tunneling diode		X	X	X	X
Battery		X	X		X

Depending on the molecules or materials that are used between the wires (the electrodes), each junction can either display the types of electrical function described below immediately on contact of the wires or the junction can have a switching function that acts to connect or disconnect the two wires together electrically. This switch can either be singly configurable or reconfigurable. In the first case, the initial state of the switch is open or closed. In the second case, by cycling the polarity and magnitude of the voltage on the switch beyond the appropriate threshold values, it is possible to reversibly oxidize or reduce the properly selected materials or molecules to close or open the switch many times. In either case, when closed, the type of electrical connection that is made between the wires depends upon the materials from which the wires (or electrodes) are fabricated as well as the identity of the molecules or materials between the wires.

Table I above shows a matrix of the various types of functions that can be obtained from various combinations of electrode materials and materials or molecules used in the junction. A resistor has a linear current-voltage characteristic, and is made by intentionally over-reducing the junction between various types of wires to essentially form a short circuit between the wires. The opposite of this process is to over-oxidize a junction, which will consume the wire in a localized region and effectively break the wire (create an open circuit) in that wire at the position of the junction. A tunneling resistor maintains a thin, approximately 2 nanometer thick, insulating barrier between wires and has an exponential current-voltage characteristic. In the case that junction molecules or materials have a sharply defined energy state inside the band gap of an electrically insulating barrier that can be accessed by electrically biasing the junction, the connection between the wires can exhibit a flow of electrical current that is dominated by the process of resonant tun-

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neling. The resonant tunneling can produce one or more inflection points in the otherwise exponential current-voltage characteristic of a tunneling resistor. A diode is a junction that passes current more easily in one direction than in the other, and thus has an asymmetry in the current-voltage characteristic for positive and negative voltages. A tunneling diode has both the positive-negative voltage asymmetry of the diode and the exponential current-voltage characteristic of the tunneling resistor. A resonant tunneling diode has a positive-negative voltage asymmetry plus it has a peak in its current-voltage characteristic, such that over a restricted range of increasing magnitude of the voltage the magnitude of the current actually decreases, a phenomenon that is known as negative differential resistivity. In general, any real junction between wires formed by the processes described above will actually have two or more of the electrical functions described, with the effective circuit elements connected in series.

Thus, the present invention may be executed with any number of metallic or semiconducting wire/molecule combinations, depending on the device properties desired from the assembled circuit.

Basic Information on Prior Art Fabrication of Wire Electrodes

Process-Defined Wires (defined as wires that are prepared by conventional electronic-circuit processing techniques; wires are typically prepared on a substrate as part of a circuit):

Metallic and semiconductor wires, with diameters ranging from several micrometers to a single micrometer (defined as micrometer-scale), or with diameters ranging from a single micrometer down to 40 nanometers (defined as sub-micrometer scale) in diameter, may be prepared using well-established art, including lithographic (optical, ultraviolet, or electron beam) technologies. These wires normally have a ribbon shape or rectangular cross section, although circular cross sections are not precluded, with the width of the wire being determined by the lithographic process used to define the wire and its height being defined by the amount of material deposited in the region defined by lithography.

Chemically-Prepared Wires (these wires are prepared by techniques other than conventional electronic processing technology; wires are typically prepared as a bulk material, rather than as part of a circuit board):

Metal and semiconductor nanowires are defined as wires with diameters below 50 nanometers (typically 2 to 20 nanometers), and with lengths in the range of 0.1 micrometers to 50 micrometers (typically 5 to 10 micrometers). These may be prepared chemically using any one of a number of techniques described in the references given below.

One example of a reported technique for the production of semiconductor nanowires of the semiconducting element germanium is to react germanium tetrachloride and phenyltrichlorogermanium with a dispersion of sodium metal in the solvent toluene, and at a

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temperature near 300°C in a closed vessel, under an inert environment, for a period of several days. That preparation produces single-crystal germanium nanowires of diameters three to thirty nanometers, and of lengths from 0.5 to 10 micrometers.

5 A second example of a reported technique for the production of semiconductor nanowires of the semiconducting element silicon, is to laser vaporize a target containing elemental silicon and iron. The target is placed in a vacuum oven at 1300°C, and an inert gas is flowed through the oven during the vaporization process. This technique produces silicon wires that have diameters in the range of 20 to 30 nanometers, and lengths ranging from 1 to 20 micrometers.

10 One example of a reported technique for the production of metallic nanowires of the metallic element gold is to electrochemically grow gold wires within the pores of an anodically etched aluminum oxide thin film. The aluminum oxide is dissolved in acidic solution, releasing the gold nanowires, which are then collected. Gold nanowires grown in this manner are characterized by diameters ranging from 20 to 30 nanometers, and lengths ranging from 0.5 to 5 micrometers.

15 Nanowires of various metallic and semiconducting materials may be prepared in a variety of fashions. Some of these devices will require doped semiconductor wires, such as doped Si.

For the case of Si wires, the wires can be doped when the wires are physically prepared. In this case, it is necessary to add the dopant into the reaction vessel as the wires are formed. For example, in the laser ablation/vacuum oven preparation technique described above, a small amount of dopant gas, such as phosphorus trihydride (PH₃) or arsenic trihydride (AsH₃) is added into the inert gas (argon, for example) that flows through the vacuum oven during the laser ablation/wire formation process.

20 Conversely, these wires can be modulation-doped by coating their surfaces with appropriate molecules – either electron-withdrawing groups (Lewis acids, such as boron trifluoride (BF₃)) or electron-donating groups (Lewis bases, such as alkylamines) to make them p-type or n-type conductors, respectively. See wire preparation routes listed below. FIG. 1b depicts a coating 20 on wire 12 and a coating 22 on wire 14. The coatings 20, 22 may be modulation-doping coatings, tunneling barriers (e.g., oxides), or other nano-scale functionally suitable materials. Alternatively, the wires 12, 14 themselves may be coated with one or more R species 16, and where the wires cross, R₂ 18 is formed. Or yet alternatively, the wires 12, 14 may be coated with molecular species 20, 22, respectively, for example, that enable one or both wires to be suspended to form colloidal suspensions, as discussed below.

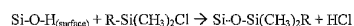
25 To dope the wires via modulation-doping, it is necessary to chemically functionalize the surface of the wires using organic or inorganic molecules that will covalently bind to the Si-O-H groups at the surface of the wires. When silicon nanowires are exposed to air, a thin surface layer (1 nm) of SiO₂ will naturally form, and at the SiO₂/air interface, the SiO₂ surface is terminated by Si-O-H bonds. Groups that will bind to or replace Si-O-H groups are not limited to but include

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R-Si(CH₃)₂(OCH₂-x), R-Si(CH₃)₂(OCH₂CH₂-x), R-Si(CH₃)₂Cl_{2-2x}, and others. In this case, R represents an organic or inorganic moiety that can contain electron-withdrawing (a Lewis acid) or electron-donating groups (a Lewis base). This chemistry of binding molecules to a SiO₂ passivated silicon surface is well established. One published example reaction for binding molecules to the surface of SiO₂ passivated silicon is:



Other semiconductor wires can be functionalized with organo-amines, organo-thiols, organo-phosphates, etc.

Apparently, no previous description of how to modulation-dope chemically synthesized semiconductor wires has yet appeared in the technical literature.

For the case of other nanowires, such as metal nanowires, the wires can be chemically functionalized with R-SH (for gold or silver wires), or R-NH₂ (for platinum wires and palladium wires), or R-COOH for other metals such as Al₂O₃-coated aluminum wires or titanium wires), where the R-group denotes some organic moiety that will lend the wire certain chemical properties – such as the property that will allow the person skilled in the art to disperse the wires, as a colloid, in a solvent. In one example, gold wires might be functionalized with dodecanethiol (C₁₂H₂₅SH). The dodecanethiol not only will provide the wires with a thin surface tunneling barrier, but will also allow for the wires to be dispersed in simple organic solvents, such as hexane or chloroform.

Basic Information on Prior Art Wire Preparation Routes

The following materials may be prepared as nanowires according to the reference listed.

Silicon: A.M. Morales et al, "A laser ablation method for the synthesis of crystalline semiconductor nanowires", *Science*, Vol. 279, pp. 208-211 (Jan. 9, 1998).

Germanium: J.R. Heath et al, "A liquid solution synthesis of single crystal germanium quantum wires", *Chemical Physics Letters*, Vol. 208, pp. 263-268 (June 11, 1993).

Metal Nanowires: V.P. Menon et al, "Fabrication and Evaluation of Nano-electrode Ensembles", *Analytical Chemistry*, Vol. 67, pp. 1920-1928 (Jul. 1, 1995).

Functionalizing Silicon: T. Vossmeier et al, "Combinatorial approaches toward patterning nanocrystals", *Journal of Applied Physics*, Vol. 84, pp. 3664-3670 (Oct. 1, 1998) (one of a number of references).

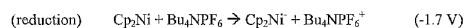
Functionalizing the Surfaces of Gold Nanostructures: D.V. Leff et al, "Thermodynamic Size Control of Au Nanocrystals: Experiment and Theory", *The Journal of Physical Chemistry*, Vol. 99, p. 7036-7041 (May 4, 1995).

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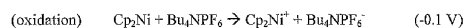
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Molecular switching components may come from any number of different classes of molecules, depending, again, on the desired properties of the device. The key requirement of the molecules is that, when they are sandwiched between two wires, they may be electrochemically modified (i.e. oxidized or reduced) by applying a voltage across the wires. When the molecular components are so modified, the net effect is that the tunneling barrier between the two wires is modified, and the rate of current flow is changed. This forms the basis of a switch that can, in turn, be used for memory, logic operations, and communication and signal routing networks. Molecular switches can include redox pairs of molecules, in which application of a voltage reduces one of the molecules and oxidizes the other. An example of such a molecular redox pair might be: nickelocene (di-cyclopentadienyl nickel), or Cp_2Ni , with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). The reaction, then, would be:



or



The nickelocene system is of particular interest in that the reduction, as probed by solution phase cyclic voltammetry, is highly asymmetric. Such asymmetry is analogous to magnetization hysteresis curves that form the basis for stable and rewriteable magnetic memory. However, in the presence of oxygen, the reduction of nickelocene is irreversible, as probed by solution phase voltammetry. In either case, reduction or oxidation of this system will modify the tunneling barrier between the two wires between which the molecules are sandwiched. Thus, this system could operate as either a reconfigurable, or a singly configurable molecular switch. For metallocene systems, see, e.g., J.D.L. Holloway et al, "Electron-transfer reactions of metallocenes: Influence of metal oxidation state on structure and reactivity", *Journal of the American Chemical Society*, Vol. 101, pp. 2038- 2044 (April 11, 1979).

The connector species 16 comprises a material that displays a significant, or measurable, hysteresis in its current-voltage curve, obtained either from solution electrochemistry or from current-voltage characteristics in a solid-state junction. Examples of such species include metallocenes, rotaxanes, pseudo-rotaxanes, and catenanes, which rely on intramolecular hydrogen bonding. While such molecules are useful for the purpose disclosed, however, simple intramolecular hydrogen bonding forces are relatively easily exceeded under certain conditions, as discussed above.

Present Invention

The present invention turns molecules into active electronic devices that can be switched with an external electric field. The general idea is to design into the molecules a rotatable middle

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segment (rotor) that has a large dipole moment (see Examples 1 and 2, below) and that links two other portions of the molecule that are immobilized (stators). Under the influence of an applied electric field, the vector dipole moment of the rotor will attempt to align parallel to the direction of the external field. However, the molecule is designed such that there are inter- and /or intra-molecular forces, such as hydrogen bonding or dipole-dipole interactions as well as steric repulsions, which stabilize the rotor in particular orientations with respect to the stators. Thus, a large field is required to cause the rotor to unlatch from its initial orientation and rotate with respect to the stators, if the direction of the applied field is opposite to that of the dipole of the rotor. Once switched into a particular orientation, the molecule will remain in that orientation until it is switched out. However, a key component of the molecule design is that there is a steric repulsion that will prevent the rotor from rotating through a complete 180 degree half cycle. Instead, the rotation is halted by the steric interaction of bulky groups on the rotor and stators at an angle of approximately 90 degrees from the initial orientation. Furthermore, this 90 degree orientation is stabilized by a different set of inter- and/or intramolecular hydrogen bonds or dipole interactions, and is thus latched into place even after the applied field is turned off. For switch molecules, this ability to latch the rotor between two states separated by approximately 90 degrees from the stators is crucial.

In the ideal case, for the orientation where the rotor and stators are all co-planar, the molecule is completely conjugated. Thus, the p, π -electrons of the molecule, through its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are delocalized over the entire molecule. This is a high conductivity (switch ON) state for the molecule. In the case where the rotor is rotated by 90 degrees with respect to the stators, the conjugation of the molecule is broken and the HOMO and LUMO are no longer delocalized over the entire molecule. This is the low conductivity (switch OFF) state of the molecule. Thus, the molecule is reversibly switchable between the ON and OFF states.

The following requirements must be met in this stator-rotor-stator model:

- (a) The molecule must have one rotor and two stator segments;
- (b) In one state of the molecule, there should be delocalized HOMOs and/or LUMOs (π -states and/or non-bonding orbitals) that extend over a large portion of the entire molecule (rotor and stators), whereas in the other state, the orbitals are localized on the rotor and stators;
- (c) The connecting unit between rotor and each stator can be a single σ -bond or at least one atom with (1) non-bonding electrons (p or other electrons), or (2) π -electrons, or (3) π -electrons and non-bonding electron(s);
- (d) The non-bonding electrons, or π -electrons, or π -electrons and non-bonding electron(s) of the rotor and stators can be localized or de-localized depending on the conformation of the molecule, while the rotor rotates when activated by an E-field;

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(e) The conformation(s) of the molecule can be E-field dependent or bi-stable;

(f) The bi-stable state(s) can be achieved by intra- or inter-molecular forces such as hydrogen bonding, Coulomb force, van der Waals force, metal ion complex or dipole inter-stabilization; and

5 (g) The band gap of the molecule will change depending on the degree of non-bonding electron, or π -electron, or π -electron and non-bonding electron de-localization of the molecule. This will change the electrical properties, such as electrical conductivity, of the molecule.

Following are two examples of this model (Examples 1 and 2):

10 The novel bi-modal molecules of the present invention are active electrical devices that can be switched with an external electric field. The general idea is to design into the molecules a rotatable middle segment (rotor) 32 that has a large dipole moment (see Examples 1 and 2) and that links two other portions of the molecule 30 that are immobilized (stators) 34, as illustrated in FIG. 2. Under the influence of an applied electric field, the vector dipole moment of the rotor 32
15 will attempt to align parallel to the direction of the external field. However, the molecule 30 is designed such that there are inter- and/or intra-molecular forces, such as hydrogen bonding or dipole-dipole interactions as well as steric repulsions, that stabilize the rotor 32 in particular orientations with respect to the stators 34. Thus, a large electric field is required to cause the rotor 32 to unlatch from its initial orientation and rotate with respect to the stators 34.

20 Once switched into a particular orientation, the molecule 30 will remain in that orientation until it is switched to a different orientation, or reconfigured. However, a key component of the molecule design is that there is a steric repulsion or hindrance that will prevent the rotor 32 from rotating through a complete 180 degree half cycle. Instead, the rotation is halted by the steric interaction of bulky groups on the rotor 32 and stators 34 at an electrically significant angle of typically
25 between 10° and 170° from the initial orientation. For the purposes of illustration, this angle is shown as 90° in the present application. Furthermore, this switching orientation may be stabilized by a different set of inter- and/or intra-molecular hydrogen bonds or dipole interactions, and is thus latched in place even after the applied field is turned off. For bi-stable switch molecules, this ability to latch the rotor 32 between two states separated by an electrically significant rotation
30 from the stators is crucial.

When the rotor 32 and stators 34 are all co-planar, the molecule is referred to as "more-conjugated". Thus, the non-bonding electrons, or π -electrons, or π -electrons and non-bonding electrons of the molecule, through its highest occupied molecular orbital (HOMO) and lowest un-occupied molecular orbital (LUMO), are delocalized over a large portion of the molecule 30. This
35 is referred to as a "more conductive state" for the molecule, or "electrical state I". In the case where the rotor 32 is rotated out of conjugation by approximately 10° to 170° with respect to the

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stators 34, the conjugation of the molecule 30 is broken and the HOMO and LUMO are localized over smaller portions of the molecule, referred to as "less-conjugated". This is a "less conductive state" of the molecule 30, or "electrical state II". Thus, the molecule 30 is reversibly switchable between two different electrical states.

5 It will be appreciated by those skilled in the art that in the ideal case, when the rotor 32 and stators 34 are completely coplanar, then the molecule is fully conjugated, and when the rotor 32 is rotated at an angle of 90° with respect to the stators 34, then the molecule is non-conjugated. However, due to thermal fluctuations, these ideal states are not fully realized, and the molecule is thus referred to as being "more-conjugated" in the former case and "less-conjugated" in the latter case.

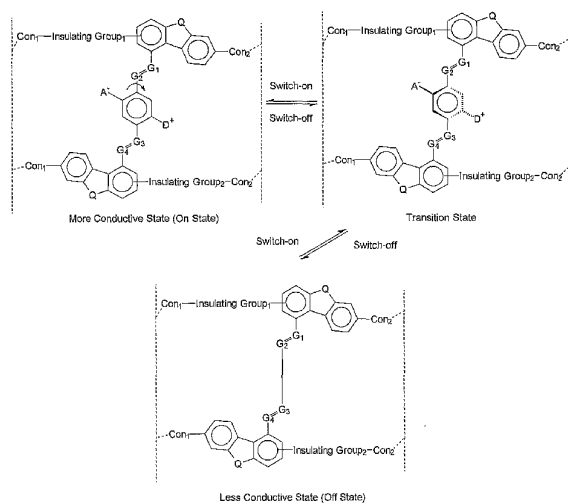
10 Examples 1 and 2 show two different orientations for switching the molecules. In Example 1, the rotation axis of the rotor is designed to be nearly perpendicular to the net current-carrying axis of the molecules, whereas in Example 2, the rotation axis is parallel to the orientation axis of the molecule. These designs allow different geometries of molecular films and electrodes to be used, depending on the desired results. Both generic and real molecular structures are presented for each example. Examples 1a and 2a are generic molecular structures to show two different orientations for switching the molecules, and Examples 1b and 2b are two real molecular structures.

15 Turning first to Example 1, this depicts a first embodiment of the bi-stable molecular mechanical device of the present invention. Example 1a below depicts a generic molecular implementation for the stator-rotor-stator model.

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Example 1a

5 where:

The letter A^- represents an Acceptor group; it is an electron-withdrawing group. It may be one of following: hydrogen, carboxylic acid or its derivatives, sulfuric acid or its derivatives, phosphoric acid or its derivatives, nitro, nitrile, hetero atoms (e.g., N, O, S, P, F, Cl, Br), or functional group with at least one of above-mentioned hetero atoms (e.g., OH, SH, NH, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

10

The letter D^+ represents a Donor group; it is an electron-donating group. It may be one of following: hydrogen, amine, OH, SH, ether, hydrocarbon (either saturated or unsaturated), or substituted hydrocarbon or functional group with at least one of hetero atom (e.g., B, Si, N, O, S, P, I). The donor is differentiated from the acceptor by that fact that it is less electronegative, or more electropositive, than the acceptor group on the molecule.

15

The letters Con_1 and Con_2 represent connecting units between a molecule and the solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (utilizing a hydrogen bond), multivalent hetero atoms (i.e., C, N, O, S, P, etc.)

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or functional groups containing these hetero atoms (e.g., NH, PH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

The letters G₁, G₂, G₃, and G₄ are bridging groups. The function of these bridging groups is to connect the stator and rotor or to connect two or more conjugated rings to achieve a desired electronic property. They may be any one of the following: hetero atoms (e.g., N, O, S, P, etc.) or functional groups with at least one of above-mentioned hetero atoms (e.g., NH or NHH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons. The connector may alternately comprise a single atom bridge such as an ether bridge with an oxygen atom, or a direct sigma bond between the rotor and stator.

10 The letter Q is used here to designate a connecting unit between two phenyl rings. It can be any one of following: S, O, NH, NR, hydrocarbon, or substituted hydrocarbon.

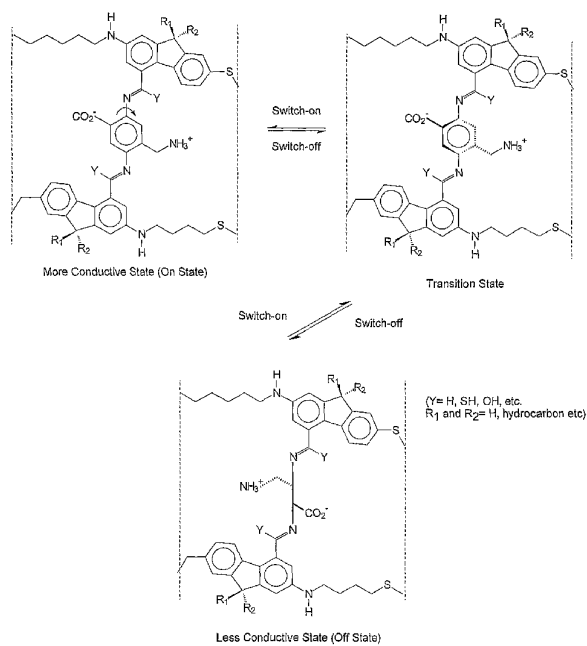
In Example 1a above, the vertical dotted lines represent other molecules or solid substrates. The direction of the switching field is perpendicular to the vertical dotted lines. Such a configuration is employed for electrical switching, and the molecule may be simply placed between the two electrodes.

15 Example 1b below is a real molecular example of the stator-rotor-stator model mentioned above:

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Example 1b

- 5 The molecule shown above (Example 1b) has been designed with the internal rotor 32 perpendicular to the orientation or current-flow axis of the entire molecule 30. In this case, the external field is applied along the orientation axis of the molecule 30 as pictured - the electrodes (vertical dotted lines) are oriented perpendicular to the plane of the paper and perpendicular to the orientation axis of the molecule 30. Application of an electric field oriented from left to right in
- 10 the diagrams will cause the rotor 32 as pictured in the upper left diagram to rotate to the position shown on the lower diagram, and vice versa. In this case, the rotor 32 as pictured in the lower diagram is not coplanar with the rest of the molecule, so this is the OFF or low conductivity state of the molecule, whereas the rotor is substantially coplanar with the rest of the molecule on the

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upper left diagram, so this is the ON or high conductivity state of the molecule. The structure shown in the upper right diagram depicts the transition state of rotation between the upper left diagram (co-planar, conjugated) and the lower diagram (central portion rotated, non-conjugated).

5 The molecule depicted in Example 1 is non-conductive (or comparatively low conductive) in the non-conjugated state. In the conjugated state, the molecule is conductive.

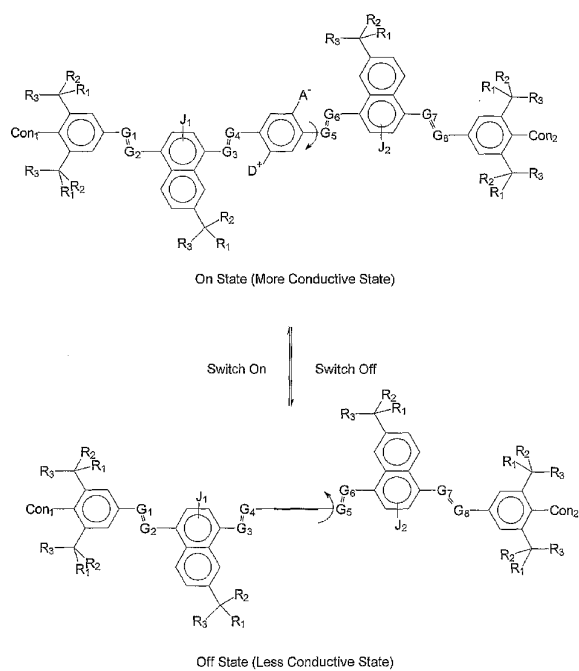
For molecules of the type shown in Example 1, a single monolayer molecular film is grown, for example using Langmuir-Blodgett techniques or self-assembled monolayers, such that the orientation axis of the molecules is perpendicular to the plane of the electrodes used to switch the molecules. Electrodes may be deposited in the manner described by Collier et al, supra, or
10 methods described in the above-referenced patent applications and issued patent.

Turning now to Example 2, this depicts a second embodiment of the bi-stable molecular mechanical device of the present invention. Example 2a below depicts a second generic molecular example for stator-rotor-stator configuration of the present invention.

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Example 2a

where:

- 5 The letter A⁻ represents an Acceptor group; it is an electron-withdrawing group. It may be one of following: hydrogen, carboxylic acid or its derivatives, sulfuric acid or its derivatives, phosphoric acid or its derivatives, nitro, nitrile, hetero atoms (e.g., N, O, S, P, F, Cl, Br), or functional group with at least one of above-mentioned hetero atoms (e.g., OH, SH, NH, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.
- 10 The letter D⁺ represents a Donor group; it is an electron-donating group. It may be one of following: hydrogen, amine, OH, SH, ether, hydrocarbon (either saturated or unsaturated), or substituted hydrocarbon or functional group with at least one of hetero atom (e.g., B, Si, I, N, O, S, P).

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The donor is differentiated from the acceptor by that fact that it is less electronegative, or more electropositive, than the acceptor group on the molecule.

The letters Con₁ and Con₂ represent connecting units between one molecule and another molecule or between a molecule and the solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (utilizing a hydrogen bond), multivalent hetero atoms (i.e., C, N, O, S, P, etc.) or functional groups containing these hetero atoms (e.g., NH, PH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

The letters R₁, R₂ and R₃ represent spacer groups built into the molecule. The function of these spacer units is to provide an appropriate 3-dimensional scaffolding to allow the molecules to pack together while providing rotational space for each rotor. They may be any one of the following: hydrogen, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

The letters G₁, G₂, G₃, G₄, G₅, G₆, G₇, and G₈ are bridging groups. The function of these bridging groups is to connect the stator and rotor or to connect two or more conjugated rings to achieve a desired electronic property. They may be any one of the following: hetero atoms (e.g., C, N, O, S, P, etc.) or functional group with at least one of above-mentioned hetero atoms (e.g., NH or NHNH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons. The connector may alternately comprise a single atom bridge such as an ether bridge with an oxygen atom, or a direct sigma bond between the rotor and stator.

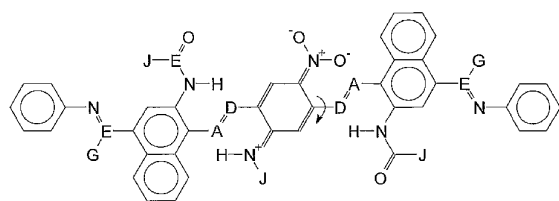
The letters J₁ and J₂ represent tuning groups built into the molecule. The function of these tuning groups (e.g., OH, NHR, COOH, CN, nitro, etc.) is to provide an appropriate functional effect (e.g. both inductive effect and resonance effects) and/or steric effects. The functional effect is to tune the band gap ($\Delta E_{HOMO/LUMO}$) of the molecule to get the desired electronic properties of the molecule. The steric effect is to tune the molecular conformation through steric hindrance, inter- or intramolecular interaction forces (e.g. hydrogen bonding, Coulomb interaction, van der Waals forces) or to provide bi- or multiple-stability of molecular orientations. They may be any one of the following: hydrogen, hetero atoms (e.g., N, O, S, P, B, F, Cl, Br, and I), functional groups with at least one of above-mentioned hetero atoms, hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

Example 2b below is a real molecular example of the stator-rotor-stator configuration mentioned above:

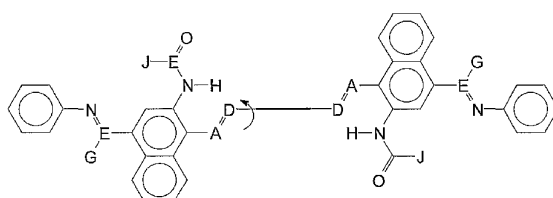
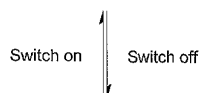
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More Conductive State (On State)



Less Conductive State (Off State)

Example 2b

- 5 The molecule shown above (Example 2b) has been designed with the internal rotor parallel to the orientation axis of the entire molecule. In this case, the external field is applied perpendicular to the molecular axis - the electrodes are oriented parallel to the long axis of the molecule and can be either perpendicular or parallel to the plane of the above model structures. For example, application of an electric field to the upper molecule shown above where the field lines are perpendicular to the molecular axis and pointing upward will cause the rotor as pictured in that diagram to rotate to approximately 90 degrees and appear edge on, as shown in the lower molecular diagram above, and vice versa. In this case, the rotor as pictured in the lower diagram is not coplanar with the rest of the molecule, so this is the OFF or low conductivity state of the molecule, whereas the rotor is coplanar with the rest of the molecule on the upper diagram, so this is the ON
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or high conductivity state of the molecule. In the diagram, the letters A, D, E, G, and J indicate sites where different chemical units can be utilized to adjust the geometrical structure of the molecule, and other chemical groups may also be used as the rotor and stators. (The letters N, H, and O retain their usual meaning.) The letters A, D, E, G, and J can be any of the following: heteroatoms (e.g., N, O, S, P, etc.), hydrocarbon (either saturated or unsaturated), or hydrocarbon with at least one of the above-mentioned heteroatoms. In addition to the foregoing, the letters G and J can be any of the following heteroatoms: hydrogen, F, Cl, Br, I, etc.

For the molecules of Example 2, the films are grown such that the molecular axis is parallel to the plane of the electrodes. This may involve films that are multiple monolayers thick. The molecules form solid-state or liquid crystals in which the large stator groups are locked into position by intermolecular interactions or direct bonding to a support structure, but the rotor is small enough to move within the lattice of the molecules. With the proper orientation of electrodes, this structure can be used to create a gated junction (transistor); i.e., one where a voltage applied to one electrode can control the current that flows between two other electrodes that are bridged by the molecules.

Although connector units are not shown in Examples 2a and 2b, such connector units, for example, -S-, depicted in Examples 1a and 1b, would be used to connect the molecule between a pair of electrodes, as depicted in Example 1. Specifically, connection is between the stator portions of the molecule and the electrodes.

Examples 1 and 2 show two different orientations for switching the molecules. However, the examples given are not to be considered limiting the invention to the specific molecular systems illustrated, but rather merely exemplary of the switching mechanism disclosed and claimed herein.

Thus, the present invention introduces a new type of switching mechanism that distinguish it from the prior art, namely, an electric field ("E-field") induced rotation of a rotatable section (rotor) of a molecule to change the band gap of the molecule. The molecule is never oxidized nor reduced in the toggling of the switch, in contrast to prior art approaches. Also, the part of the molecule that moves is quite small, so the switching time is expected to be quite fast. Also, the molecules are much simpler and thus easier and cheaper to make than the rotaxanes, catenanes, and related compounds.

The technology disclosed and claimed herein for forming crossed wires (micro-meter or nanometer) may be used to perform a variety of functions and to form a variety of useful devices and circuits for implementing computing on a microscale and even on a nanoscale. For example, applications include molecular wire crossbar interconnects (MWCI) for signal routing and communications, molecular wire crossbar memory (U.S. Patent 6,128,214), molecular wire crossbar logic (MWCL) employing programmable logic arrays, a demultiplexer for a molecular wire crossbar network, molecular wire transistors, and pixel arrays for displays.

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As illustrated in FIG. 3, the switch 10 of the present invention can be replicated in a two-dimensional array to form a plurality, or array, 60 of switches to form a crossbar switch. FIG. 3 depicts a 6x6 array 60, but the invention is not so limited to the particular number of elements, or switches, in the array. Access to a single point, e.g., 2b, is done by impressing voltage on wires 2 and 5 h to cause a change in the state of the molecular species 18 at the junction thereof, as described above. Thus, access to each junction is readily available for configuring only those pre-selected junctions in accordance with the teachings herein. Details of the operation of the crossbar switch array 60 are further discussed in above-referenced U.S. Patent 6,128,214.

10

INDUSTRIAL APPLICABILITY

The field-switchable molecules disclosed herein are expected to find use in micro-scale and nano-scale electronic devices.

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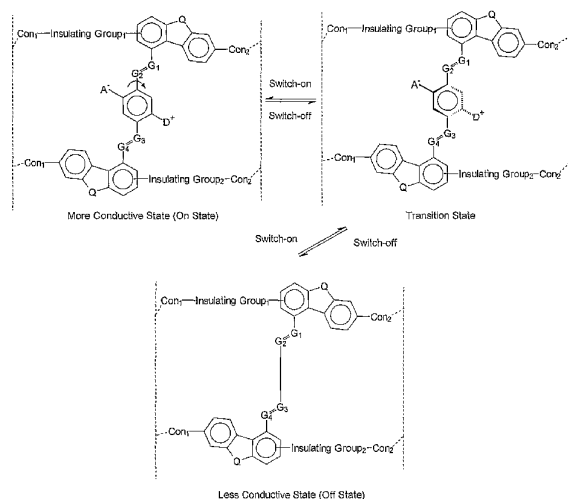
CLAIMSWhat Is Claimed Is:

- 5 1. A bi-stable molecular mechanical device (60) comprising a molecular system (30) configured within an electric field generated by a pair of electrodes (12, 14) and electrically connected thereto, said molecular system (30) having one rotor portion (32) connected between two stator portions (34), wherein said rotor portion (32) rotates with respect to said stator portions (34) between at least two different states upon application of said electric field, thereby inducing a band
- 10 gap change in said molecular system (30), wherein in a first state, there is extended conjugation over at least most of said molecular system (30), resulting in a relatively smaller band gap, and wherein in a second state, said extended conjugation is destroyed, resulting in a relatively larger band gap.
- 15 2. The molecular device (60) of Claim 1 wherein said molecular system (30) has an orientation axis and wherein said rotor portion (32) is oriented perpendicular to said orientation axis, with said external electric field applied parallel to said orientation axis.
- 20 3. The molecular device (60) of Claim 2 wherein said molecular system (30) comprises:

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where

A⁻ is an Acceptor group comprising an electron-withdrawing group selected from the group consisting of: (a) hydrogen, (b) carboxylic acid and its derivatives, (c) sulfuric acid and its derivatives, (d) phosphoric acid and its derivatives, (e) nitro, (f) nitrile, (g) hetero atoms selected from the group consisting of N, O, S, P, F, Cl, and Br, (h) functional group with at least one of said hetero atoms, (i) saturated or unsaturated hydrocarbons, and (j) substituted hydrocarbons;

D⁺ is a Donor group comprising an electron-donating group selected from the group consisting of: (a) hydrogen, (b) amines, (c) OH, (d) SH, (e) ethers, (f) saturated or unsaturated hydrocarbons, (h) substituted hydrocarbons, and (i) functional groups with at least one of hetero atom selected from the group consisting of B, Si, N, O, S, P, and I, wherein said Donor group is more electropositive than said Acceptor group;

Con₁ and Con₂ are connecting units between a molecule and a solid substrate selected from the group consisting of a metal electrode, an inorganic substrate, and an organic substrate, said connecting units independently selected from the group consisting of: (a) hydrogen (utilizing a hydrogen bond), (b) multivalent hetero atoms selected from the group consisting of C, N, O, S, and P, (c) functional groups containing said hetero atoms, (d) saturated or unsaturated hydrocarbons, and (d) substituted hydrocarbons;

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G₁, G₂, G₃, and G₄ are bridging groups for connecting said stator to each rotor or to connect two or more conjugated rings to achieve a desired electronic property, said bridging groups selected from the group consisting of: (a) hetero atoms selected from the group consisting of N, O, S, and P, (b) functional groups with at least one of said hetero atoms, (c) saturated or unsaturated hydrocarbons, (d) substituted hydrocarbons, (e) a single atom bridge, and (f) a direct sigma bond between said rotor and each stator; and

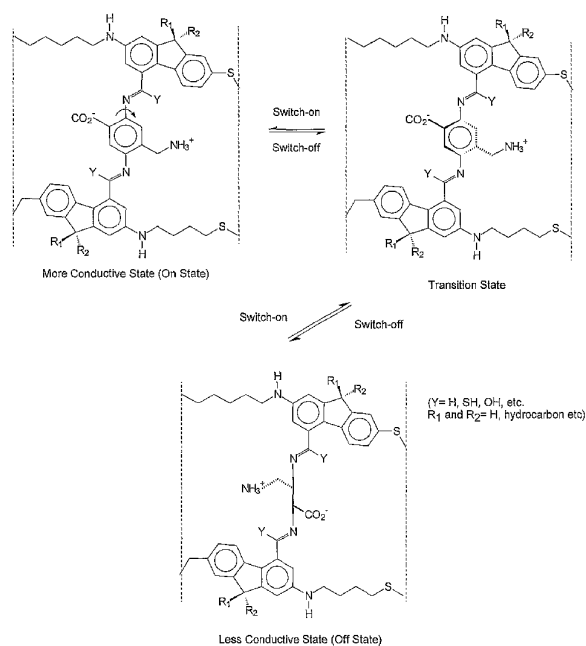
Q is a connecting unit between two phenyl rings and is selected from the group consisting of: (a) S, (b) O, (c) NH, (d) NR, (e) hydrocarbon, and (f) substituted hydrocarbon, and where the vertical dashed lines represent said solid substrate to which said molecule is electrically attached.

4. The molecular device (60) of Claim 3 wherein said molecular system (30) comprises:

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where:

- R₁ and R₂ are independently hydrogen or hydrocarbon; and
 5 Y is selected from the group consisting of hydrogen, OH, and SH.

5. The molecular device (60) of Claim 1 wherein said molecular system (30) has an orientation axis and wherein said rotor portion (32) is oriented parallel to said orientation axis, with said external electric field applied perpendicular to said orientation axis.

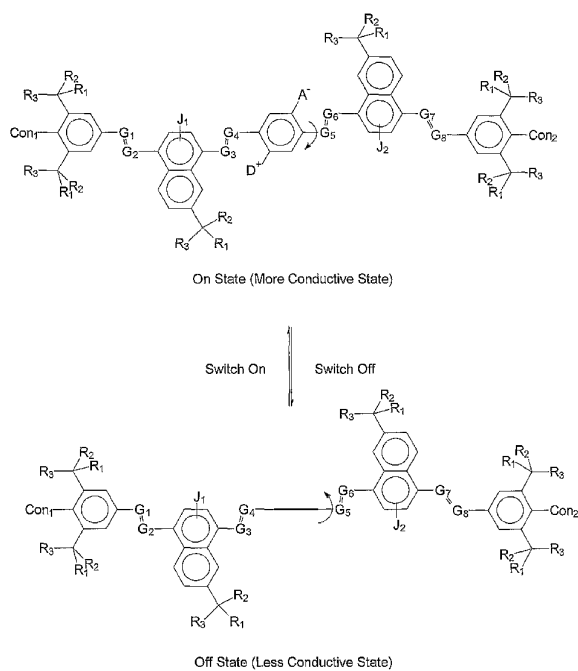
10

6. The molecular device (60) of Claim 5 wherein said molecular system (30) comprises:

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where:

- 5 A^- is an Acceptor group comprising an electron-withdrawing group selected from the group consisting of: (a) hydrogen, (b) carboxylic acid and its derivatives, (c) sulfuric acid and its derivatives, (d) phosphoric acid and its derivatives, (e) nitro, (f) nitrile, (g) hetero atoms selected from the group consisting of N, O, S, P, F, Cl, and Br, (h) functional groups with at least one of said hetero atoms, (i) saturated or unsaturated hydrocarbons, and (j) substituted hydrocarbons;

- 10 D^+ is a Donor group comprising an electron-donating group selected from the group consisting of: (a) hydrogen, (b) amines, (c) OH , (d) SH , (e) ethers, (f) saturated and unsaturated hydrocarbons, (g) substituted hydrocarbons, and (i) functional groups with at least one of hetero

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atom selected from the group consisting of B, Si, N, O, S, P, and I, wherein said Donor group is more electropositive than said Acceptor group;

Con₁ and Con₂ are connecting units between one molecule and another molecule or between a molecule and a solid substrate selected from the group consisting of a metal electrode, an inorganic substrate, and an organic substrate, said connecting units independently selected from the group consisting of: (a) hydrogen (utilizing a hydrogen bond), (b) multivalent hetero atoms selected from the group consisting of C, N, O, S, and P, (c) functional groups containing said hetero atoms, (d) saturated or unsaturated hydrocarbons, and (e) substituted hydrocarbons;

R₄, R₂ and R₃ are spacing groups for providing an appropriate 3-dimensional scaffolding to allow molecules to pack together while providing rotational space for each rotor, said spacing groups selected from the group consisting of: (a) hydrogen, (b) saturated or unsaturated hydrocarbon, and (c) substituted hydrocarbon;

G₁, G₂, G₃, G₄, G₅, G₆, G₇, and G₈ are bridging groups for connecting said stator to each rotor or to connect two or more conjugated rings to achieve a desired electronic property, said bridging groups selected from the group consisting of: (a) hetero atoms selected from the group consisting of N, O, S, and P, (b) functional groups with at least one of said hetero atoms, (c) saturated or unsaturated hydrocarbons, (d) substituted hydrocarbons, (e) a single atom bridge, and (f) a direct sigma bond between said rotor and each stator; and

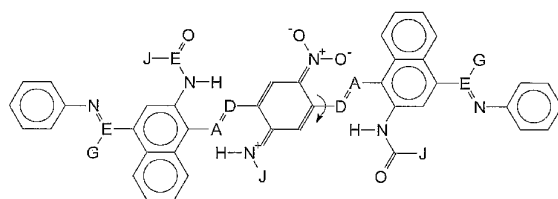
J₁ and J₂ are tuning groups to provide at least one appropriate functional effect selected from the group consisting of inductive effects, resonance effects, and steric effects, said tuning groups being selected from the group consisting of: (a) hydrogen, (b) hetero atoms selected from the group consisting of N, O, S, P, B, F, Cl, Br and I, (c) functional groups with at least one of said hetero atoms, (d) saturated or unsaturated hydrocarbons, and (e) substituted hydrocarbons;

7. The molecular device (60) of Claim 6 wherein said molecular system (30) comprises:

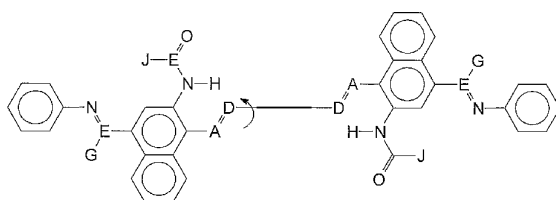
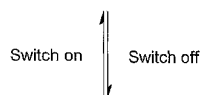
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More Conductive State (On State)



Less Conductive State (Off State)

wherein the letters A, D, E, G, and J indicate sites where different chemical units can be utilized to adjust geometrical structure and optical properties of said molecular system and have generic designations as follows: A, D, E, G, and J are independently selected from the group consisting of heteroatoms, hydrocarbons (either saturated or unsaturated), and hydrocarbons with at least one said heteroatom, and where in addition to the foregoing, the letters G and J are independently selected from the group consisting of hydrogen, F, Cl, Br, and I.

8. The molecular device (60) of Claim 1 comprising a crossed-wire device (10) comprising a pair of crossed wires (12, 14) that form a junction (18) where one wire (14) crosses another (12) at an angle other than zero degrees and at least one connector species (16) connecting said pair of crossed wires (12, 14) in said junction (18), said junction (18) having a functional dimension in

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nanometers, wherein said at least one connector species (16) comprises said molecular system (30).

5 9. The molecular device (60) of Claim 8 wherein said crossed-wire device (10) is selected from the group consisting of memories, logic devices, multiplexers, demultiplexers, configurable interconnects for integrated circuits, field-programmable gate arrays (FPGAs), cross-bar switches, and communication devices.

10 10. The molecular device (60) of Claim 1 wherein said molecular system (30) is connected to said pair of electrodes (12, 14) by connector units.

11. A bi-stable molecular system (30) comprising the molecular system (30) of Claim 1.

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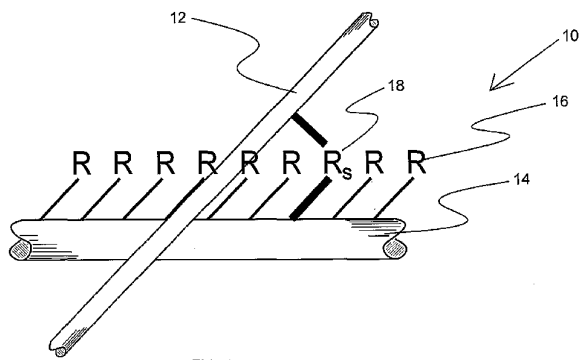


FIG. 1a

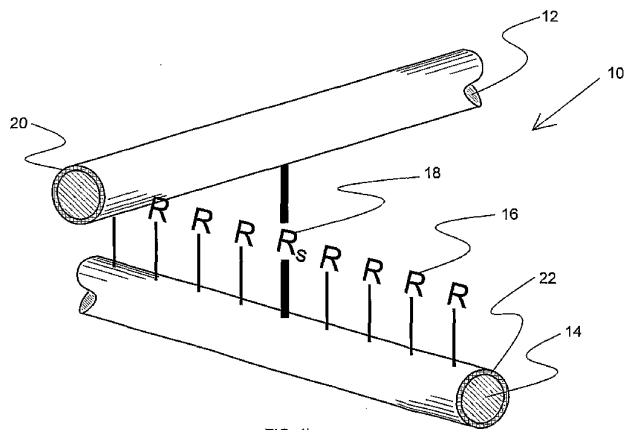


FIG. 1b

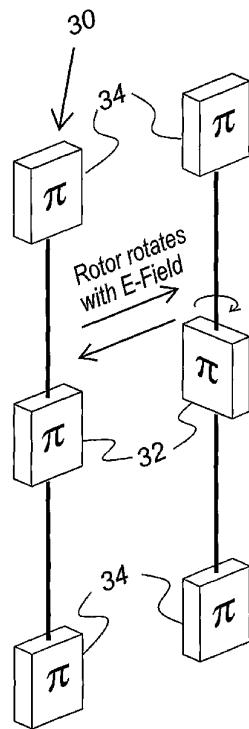


FIG. 2

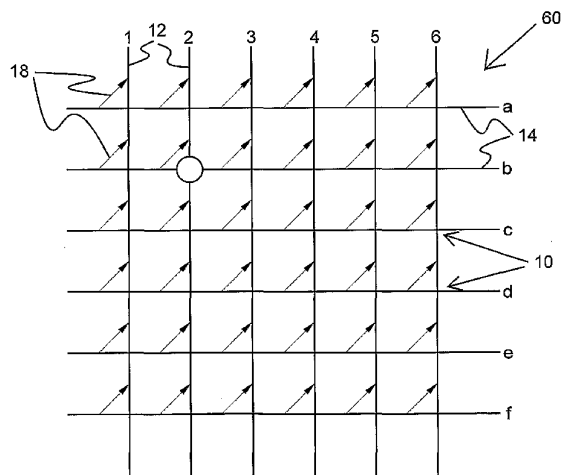


FIG. 3

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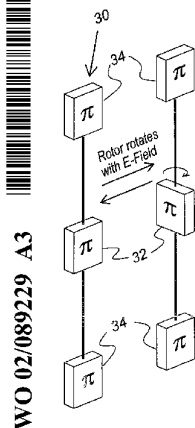
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(54) Title: BISTABLE MOLECULAR MECHANICAL DEVICES WITH A MIDDLE ROTATING SEGMENT ACTIVATED BY AN ELECTRIC FIELD FOR ELECTRONIC SWITCHING, GATING, AND MEMORY APPLICATIONS



(57) Abstract: A molecular system (30) is provided for electric field activated switches, such as a crossed-wire device (10) or a pair of electrodes (12, 14) to which the molecular system (30) is linked by linking moieties. The cross-wire device (10) comprises a pair of crossed wires (12, 14) that form a junction (18) where one wire (14) crosses another (12) at an angle other than zero degrees and at least one connector species (16) connecting the pair of crossed wires (12, 14) in the junction (18). The connector species (16) comprises the molecular system (30), which has an electric field induced band gap change, and thus a change in its electrical conductivity, that occurs via one a molecular conformation change, based on a rotor/stator construction of the molecular system (30), involving a rotating portion (rotor) (32) connected between the stationary portions (stators) (34). Nanometer-scale reversible electronic switches (10) are thus provided that can be assembled easily to make cross-bar circuits (60), which provide memory, logic, and communication functions.

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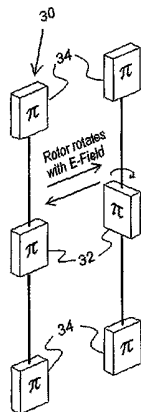
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Sunnyvale, CA 94086 (US). WILLIAMS, R. Stanley; 105For two-letter codes and other abbreviations, refer to the "Guid-
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10 BISTABLE MOLECULAR MECHANICAL DEVICES WITH A
MIDDLE ROTATING SEGMENT ACTIVATED BY AN ELECTRIC
FIELD FOR ELECTRONIC SWITCHING, GATING, AND
MEMORY APPLICATIONS

15 TECHNICAL FIELD

The present invention relates generally to electronic devices whose functional length scales are measured in nanometers, and, more particularly, to classes of molecules that provide electronic switching. Electronic devices both of micrometer and nanometer scale may be constructed in accordance with the teachings herein.

20

BACKGROUND ART

25 The area of molecular electronics is in its infancy. To date, there have been two convincing demonstrations of molecules as electronic switches published in the technical literature; see, C.F. Collier et al., Science, Vol. 285, pp. 391-394 (16 July 1999) and C.F. Collier et al., Science, Vol. 289, pp. 1172-1175 (18 August 2000), but there is a great deal of speculation and interest within the scientific community surrounding this topic. In the published work, a molecule called a rotaxane or a catenane was trapped between two metal electrodes and caused to switch from an ON state to an OFF state by the application of a positive bias across the molecule. The ON and OFF states differed in resistivity by about a factor of 100 and 5, respectively, for the rotaxane and catenane.

30 The primary problem with the rotaxane was that it is an irreversible switch. It can only be toggled once. Thus, it can be used in a programmable read-only memory (PROM), but not in a ROM-like device nor in a reconfigurable system, such as a defect-tolerant communications and logic network. In addition, the rotaxane requires an oxidation and/or reduction reaction to occur

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before the switch can be toggled. This requires the expenditure of a significant amount of energy to toggle the switch. In addition, the large and complex nature of rotaxanes and related compounds potentially makes the switching times of the molecules slow. The primary problems with the catenanes are small ON-to-OFF ratio and a slow switching time.

5 Thus, what is needed is a molecular system that avoids chemical oxidation and/or reduction, permits reasonably rapid switching from a first state to a second, is reversible to permit the fabrication of ROM-like devices, and can be used in a variety of electronic devices.

DISCLOSURE OF INVENTION

10

In accordance with the present invention, a molecular system is provided for nanometer-scale reversible electronic switches, specifically, electric field activated molecular switches that have an electric field induced band gap change that occurs via a molecular conformation change or an isomerization. Changing of extended conjugation via chemical bonding change to change the band gap is accomplished by providing the molecular system with one rotating portion (rotor) and two stationary portions (stators), between which the rotor is attached.

15 The present invention provides nanometer-scale reversible electronic switches that can be assembled easily to make cross-bar and other circuits. The cross-bar circuits have been described in the above-listed series of patent applications and issued patent. The circuits provide memory, logic and communications functions. One example of the electronic switches is the so-called crossed-wire device, which comprises a pair of crossed wires that form a junction where one wire crosses another at an angle other than zero degrees and at least one connector species connecting the pair of crossed wires in the junction. The junction has a functional dimension in nanometers or larger for multilayers. The connector species comprises the molecular system disclosed and claimed herein.

25 The present invention introduces a new type of switching mechanism, namely, an electric field induced rotation of a rotatable middle section (rotor) of a molecule. Thus, the molecule is neither oxidized nor reduced in the toggling of the switch, which avoids the necessity of breaking chemical bonds and potentially initiating a nonreversible reaction. Also, the part of the molecule that moves is quite small, so the switching time should be very fast. Also, the molecules are much simpler and thus easier and cheaper to make than the rotaxanes and related compounds.

30 The devices of the present invention are generically considered to be electric field devices, and are to be distinguished from earlier embodiments (described in the above-mentioned related patent applications and patent) that are directed to electrochemical devices.

35 The molecular system of the present invention is expected to find use in a variety of applications, including, but not limited to, memories, logic devices, multiplexers, demultiplexers,

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configurable interconnects for integrated circuits, field-programmable gate arrays (FPGAs), cross-bar switches, and communication devices, such as cellular phones, mobile appliances, and PDAs.

BRIEF DESCRIPTION OF THE DRAWINGS

5

FIG. 1a is a schematic representation of two crossed wires, with at least one molecule at the intersection of the two wires;

FIG. 1b is a perspective elevational view, depicting the device shown in FIG. 1a;

FIG. 2 is a schematic model depicting an E-field-induced band gap change via molecular
10 conformation change (rotor/stator type of model); and

FIG. 3 is a schematic representation of a two-dimensional array of switches of the present invention, depicting a 6x6 crossbar switch.

BEST MODES FOR CARRYING OUT THE INVENTION

15

Definitions

As used herein, the term "self-aligned" as applied to "junction" means that the junction that forms the switch and/or other electrical connection between two wires is created wherever two wires, either of which may be coated or functionalized, cross each other, because it is the act
20 of crossing that creates the junction.

The term "self-assembled" as used herein refers to a system that naturally adopts some geometric pattern because of the identity of the components of the system; the system achieves at least a local minimum in its energy by adopting this configuration.

The term "singly configurable" means that a switch can change its state only once via an
25 irreversible process such as an oxidation or reduction reaction; such a switch can be the basis of a programmable read-only memory (PROM), for example.

The term "reconfigurable" means that a switch can change its state multiple times via a reversible process such as an oxidation or reduction; in other words, the switch can be opened and closed multiple times, such as the memory bits in a random access memory (RAM).

The term "bi-stable" as applied to a molecule means a molecule having two relatively low
30 energy states separated by an energy (or activation) barrier. The molecule may be either irreversibly switched from one state to the other (singly configurable) or reversibly switched from one state to the other (reconfigurable).

Micron-scale dimensions refers to dimensions that range from 1 micrometer to a few mi-
35 crometers in size.

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Sub-micron scale dimensions refers to dimensions that range from 1 micrometer down to 0.05 micrometers.

Nanometer scale dimensions refers to dimensions that range from 0.1 nanometers to 50 nanometers (0.05 micrometers).

5 Micron-scale and submicron-scale wires refers to rod or ribbon-shaped conductors or semiconductors with widths or diameters having the dimensions of 0.05 to 10 micrometers, heights that can range from a few tens of nanometers to a micrometer, and lengths of several micrometers and longer.

10

Basic Information on Prior Art Crossed Wire Switches

The essential device features are shown in FIGS. 1a-1b and are discussed in greater detail in the above-related patent applications and patent. A crossed wire switch 10 comprises two wires 12, 14, each either a metal or semiconductor wire, that are crossed at some non-zero angle. In between those wires is a layer of molecules or molecular compounds 16, denoted R in FIGS. 1a and 1b. The particular molecules 18 (denoted R_n) that are sandwiched at the intersection of the two wires 12, 14 are identified as switch molecules, also interchangeable referred to herein as a junction. When an appropriate voltage is applied across the wires, the switch molecules are either oxidized or reduced. When a molecule is oxidized (reduced), then a second species is reduced (oxidized) so that charge is balanced. These two species are then called a redox pair. One example of this device would be for one molecule to be reduced, and then a second molecule (the other half of the redox pair) is oxidized. In another example, a molecule is reduced, and one of the wires is oxidized. In a third example, a molecule is oxidized, and one of the wires is reduced. In a fourth example, one wire is oxidized, and an oxide associated with the other wire is reduced. In all cases, oxidation or reduction will affect the tunneling distance or the tunneling barrier height between the two wires, thereby exponentially altering the rate of charge transport across the wire junction, and serving as the basis for a switch.

25 The electrical tasks performed by these devices are largely determined by the types of wires (electrodes) and the interwire materials that are used. Table I presents the various types of devices that might be fabricated from various combinations of the wires 12, 14 in FIGS 1a-1b.

30

Table I. Wire (Electrode) Materials

Device Type	Metal-metal (same)	Metal-metal (different)	Metal-semiconductor	Semiconductor-Semiconductor (p-n junction)	Semiconductor-semiconductor (heterojunction)
Resistor	X	X	X		

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Tunneling resistor	X	X	X		
Resonant tunneling resistor	X	X	X		
Diode		X	X	X	X
Tunneling diode		X	X	X	X
Resonant tunneling diode		X	X	X	X
Battery		X	X		X

Depending on the molecules or materials that are used between the wires (the electrodes), each junction can either display the types of electrical function described below immediately on contact of the wires or the junction can have a switching function that acts to connect or disconnect the two wires together electrically. This switch can either be singly configurable or reconfigurable. In the first case, the initial state of the switch is open or closed. In the second case, by cycling the polarity and magnitude of the voltage on the switch beyond the appropriate threshold values, it is possible to reversibly oxidize or reduce the properly selected materials or molecules to close or open the switch many times. In either case, when closed, the type of electrical connection that is made between the wires depends upon the materials from which the wires (or electrodes) are fabricated as well as the identity of the molecules or materials between the wires.

Table I above shows a matrix of the various types of functions that can be obtained from various combinations of electrode materials and materials or molecules used in the junction. A resistor has a linear current-voltage characteristic, and is made by intentionally over-reducing the junction between various types of wires to essentially form a short circuit between the wires. The opposite of this process is to over-oxidize a junction, which will consume the wire in a localized region and effectively break the wire (create an open circuit) in that wire at the position of the junction. A tunneling resistor maintains a thin, approximately 2 nanometer thick, insulating barrier between wires and has an exponential current-voltage characteristic. In the case that junction molecules or materials have a sharply defined energy state inside the band gap of an electrically insulating barrier that can be accessed by electrically biasing the junction, the connection between the wires can exhibit a flow of electrical current that is dominated by the process of resonant tun-

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neling. The resonant tunneling can produce one or more inflection points in the otherwise exponential current-voltage characteristic of a tunneling resistor. A diode is a junction that passes current more easily in one direction than in the other, and thus has an asymmetry in the current-voltage characteristic for positive and negative voltages. A tunneling diode has both the positive-negative voltage asymmetry of the diode and the exponential current-voltage characteristic of the tunneling resistor. A resonant tunneling diode has a positive-negative voltage asymmetry plus it has a peak in its current-voltage characteristic, such that over a restricted range of increasing magnitude of the voltage the magnitude of the current actually decreases, a phenomenon that is known as negative differential resistivity. In general, any real junction between wires formed by the processes described above will actually have two or more of the electrical functions described, with the effective circuit elements connected in series.

Thus, the present invention may be executed with any number of metallic or semiconducting wire/molecule combinations, depending on the device properties desired from the assembled circuit.

15

Basic Information on Prior Art Fabrication of Wire Electrodes

Process-Defined Wires (defined as wires that are prepared by conventional electronic-circuit processing techniques; wires are typically prepared on a substrate as part of a circuit):

Metallic and semiconductor wires, with diameters ranging from several micrometers to a single micrometer (defined as micrometer-scale), or with diameters ranging from a single micrometer down to 40 nanometers (defined as sub-micrometer scale) in diameter, may be prepared using well-established art, including lithographic (optical, ultraviolet, or electron beam) technologies. These wires normally have a ribbon shape or rectangular cross section, although circular cross sections are not precluded, with the width of the wire being determined by the lithographic process used to define the wire and its height being defined by the amount of material deposited in the region defined by lithography.

Chemically-Prepared Wires (these wires are prepared by techniques other than conventional electronic processing technology; wires are typically prepared as a bulk material, rather than as part of a circuit board):

Metal and semiconductor nanowires are defined as wires with diameters below 50 nanometers (typically 2 to 20 nanometers), and with lengths in the range of 0.1 micrometers to 50 micrometers (typically 5 to 10 micrometers). These may be prepared chemically using any one of a number of techniques described in the references given below.

One example of a reported technique for the production of semiconductor nanowires of the semiconducting element germanium is to react germanium tetrachloride and phenyltrichlorogermanium with a dispersion of sodium metal in the solvent toluene, and at a

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temperature near 300°C in a closed vessel, under an inert environment, for a period of several days. That preparation produces single-crystal germanium nanowires of diameters three to thirty nanometers, and of lengths from 0.5 to 10 micrometers.

5 A second example of a reported technique for the production of semiconductor nanowires of the semiconducting element silicon, is to laser vaporize a target containing elemental silicon and iron. The target is placed in a vacuum oven at 1300°C, and an inert gas is flowed through the oven during the vaporization process. This technique produces silicon wires that have diameters in the range of 20 to 30 nanometers, and lengths ranging from 1 to 20 micrometers.

10 One example of a reported technique for the production of metallic nanowires of the metallic element gold is to electrochemically grow gold wires within the pores of an anodically etched aluminum oxide thin film. The aluminum oxide is dissolved in acidic solution, releasing the gold nanowires, which are then collected. Gold nanowires grown in this manner are characterized by diameters ranging from 20 to 30 nanometers, and lengths ranging from 0.5 to 5 micrometers.

15 Nanowires of various metallic and semiconducting materials may be prepared in a variety of fashions. Some of these devices will require doped semiconductor wires, such as doped Si.

For the case of Si wires, the wires can be doped when the wires are physically prepared. In this case, it is necessary to add the dopant into the reaction vessel as the wires are formed. For example, in the laser ablation/vacuum oven preparation technique described above, a small amount of dopant gas, such as phosphorus trihydride (PH₃) or arsenic trihydride (AsH₃) is added into the inert gas (argon, for example) that flows through the vacuum oven during the laser ablation/wire formation process.

20 Conversely, these wires can be modulation-doped by coating their surfaces with appropriate molecules – either electron-withdrawing groups (Lewis acids, such as boron trifluoride (BF₃)) or electron-donating groups (Lewis bases, such as alkylamines) to make them p-type or n-type conductors, respectively. See wire preparation routes listed below. FIG. 1b depicts a coating 20 on wire 12 and a coating 22 on wire 14. The coatings 20, 22 may be modulation-doping coatings, tunneling barriers (e.g., oxides), or other nano-scale functionally suitable materials. Alternatively, the wires 12, 14 themselves may be coated with one or more R species 16, and where the wires cross, R₄ 18 is formed. Or yet alternatively, the wires 12, 14 may be coated with molecular species 20, 22, respectively, for example, that enable one or both wires to be suspended to form colloidal suspensions, as discussed below.

25 To dope the wires via modulation-doping, it is necessary to chemically functionalize the surface of the wires using organic or inorganic molecules that will covalently bind to the Si-O-H groups at the surface of the wires. When silicon nanowires are exposed to air, a thin surface layer (1 nm) of SiO₂ will naturally form, and at the SiO₂/air interface, the SiO₂ surface is terminated by Si-O-H bonds. Groups that will bind to or replace Si-O-H groups are not limited to but include

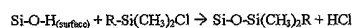
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R-Si(CH₃)₃(OCH₃)₂, R-Si(CH₃)₂(OCH₂CH₃)₂, R-Si(CH₃)₂Cl₂, and others. In this case, R represents an organic or inorganic moiety that can contain electron-withdrawing (a Lewis acid) or electron-donating groups (a Lewis base). This chemistry of binding molecules to a SiO₂ passivated silicon surface is well established. One published example reaction for binding molecules to the surface of SiO₂ passivated silicon is:



Other semiconductor wires can be functionalized with organo-amines, organo-thiols, organo-phosphates, etc.

Apparently, no previous description of how to modulation-dope chemically synthesized semiconductor wires has yet appeared in the technical literature.

For the case of other nanowires, such as metal nanowires, the wires can be chemically functionalized with R-SH (for gold or silver wires), or R-NH₂ (for platinum wires and palladium wires), or R-CO₂H for other metals such as Al₂O₃-coated aluminum wires or titanium wires), where the R-group denotes some organic moiety that will lend the wire certain chemical properties – such as the property that will allow the person skilled in the art to disperse the wires, as a colloid, in a solvent. In one example, gold wires might be functionalized with dodecanethiol (C₁₂H₂₅SH). The dodecanethiol not only will provide the wires with a thin surface tunneling barrier, but will also allow for the wires to be dispersed in simple organic solvents, such as hexane or chloroform.

Basic Information on Prior Art Wire Preparation Routes

The following materials may be prepared as nanowires according to the reference listed.

Silicon: A.M. Morales et al, "A laser ablation method for the synthesis of crystalline semiconductor nanowires", *Science*, Vol. 279, pp. 208-211 (Jan. 9, 1998).

Germanium: J.R. Heath et al, "A liquid solution synthesis of single crystal germanium quantum wires", *Chemical Physics Letters*, Vol. 208, pp. 263-268 (June 11, 1993).

Metal Nanowires: V.P. Menon et al, "Fabrication and Evaluation of Nano-electrode Ensembles", *Analytical Chemistry*, Vol. 67, pp. 1920-1928 (Jul. 1, 1995).

Functionalizing Silicon: T. Vossmeier et al, "Combinatorial approaches toward patterning nanocrystals", *Journal of Applied Physics*, Vol. 84, pp. 3664-3670 (Oct. 1, 1998) (one of a number of references).

Functionalizing the Surfaces of Gold Nanostructures: D.V. Leff et al, "Thermodynamic Size Control of Au Nanocrystals: Experiment and Theory", *The Journal of Physical Chemistry*, Vol. 99, p. 7036-7041 (May 4, 1995).

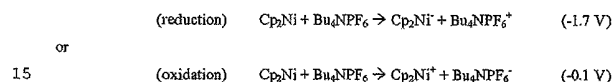
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Molecular switching components may come from any number of different classes of molecules, depending, again, on the desired properties of the device. The key requirement of the molecules is that, when they are sandwiched between two wires, they may be electrochemically modified (i.e. oxidized or reduced) by applying a voltage across the wires. When the molecular components are so modified, the net effect is that the tunneling barrier between the two wires is modified, and the rate of current flow is changed. This forms the basis of a switch that can, in turn, be used for memory, logic operations, and communication and signal routing networks. Molecular switches can include redox pairs of molecules, in which application of a voltage reduces one of the molecules and oxidizes the other. An example of such a molecular redox pair might be: nickelocene (di-cyclopentadienyl nickel), or Cp_2Ni , with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). The reaction, then, would be:



The nickelocene system is of particular interest in that the reduction, as probed by solution phase cyclic voltammetry, is highly asymmetric. Such asymmetry is analogous to magnetization hysteresis curves that form the basis for stable and rewriteable magnetic memory. However, in the presence of oxygen, the reduction of nickelocene is irreversible, as probed by solution phase voltammetry. In either case, reduction or oxidation of this system will modify the tunneling barrier between the two wires between which the molecules are sandwiched. Thus, this system could operate as either a reconfigurable, or a singly configurable molecular switch. For metallocene systems, see, e.g., J.D.L. Holloway et al, "Electron-transfer reactions of metallocenes: Influence of metal oxidation state on structure and reactivity", *Journal of the American Chemical Society*, Vol. 101, pp. 2038- 2044 (April 11, 1979).

The connector species 16 comprises a material that displays a significant, or measurable, hysteresis in its current-voltage curve, obtained either from solution electrochemistry or from current-voltage characteristics in a solid-state junction. Examples of such species include metallocenes, rotaxanes, pseudo-rotaxanes, and catenanes, which rely on intramolecular hydrogen bonding. While such molecules are useful for the purpose disclosed, however, simple intramolecular hydrogen bonding forces are relatively easily exceeded under certain conditions, as discussed above.

Present Invention

The present invention turns molecules into active electronic devices that can be switched with an external electric field. The general idea is to design into the molecules a rotatable middle

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segment (rotor) that has a large dipole moment (see Examples 1 and 2, below) and that links two other portions of the molecule that are immobilized (stators). Under the influence of an applied electric field, the vector dipole moment of the rotor will attempt to align parallel to the direction of the external field. However, the molecule is designed such that there are inter- and /or intra-molecular forces, such as hydrogen bonding or dipole-dipole interactions as well as steric repulsions, which stabilize the rotor in particular orientations with respect to the stators. Thus, a large field is required to cause the rotor to unlatch from its initial orientation and rotate with respect to the stators, if the direction of the applied field is opposite to that of the dipole of the rotor. Once switched into a particular orientation, the molecule will remain in that orientation until it is switched out. However, a key component of the molecule design is that there is a steric repulsion that will prevent the rotor from rotating through a complete 180 degree half cycle. Instead, the rotation is halted by the steric interaction of bulky groups on the rotor and stators at an angle of approximately 90 degrees from the initial orientation. Furthermore, this 90 degree orientation is stabilized by a different set of inter- and/or intramolecular hydrogen bonds or dipole interactions, and is thus latched into place even after the applied field is turned off. For switch molecules, this ability to latch the rotor between two states separated by approximately 90 degrees from the stators is crucial.

In the ideal case, for the orientation where the rotor and stators are all co-planar, the molecule is completely conjugated. Thus, the p, π -electrons of the molecule, through its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are delocalized over the entire molecule. This is a high conductivity (switch ON) state for the molecule. In the case where the rotor is rotated by 90 degrees with respect to the stators, the conjugation of the molecule is broken and the HOMO and LUMO are no longer delocalized over the entire molecule. This is the low conductivity (switch OFF) state of the molecule. Thus, the molecule is reversibly switchable between the ON and OFF states.

The following requirements must be met in this stator-rotor-stator model:

- (a) The molecule must have one rotor and two stator segments;
- (b) In one state of the molecule, there should be delocalized HOMOs and/or LUMOs (π -states and/or non-bonding orbitals) that extend over a large portion of the entire molecule (rotor and stators), whereas in the other state, the orbitals are localized on the rotor and stators;
- (c) The connecting unit between rotor and each stator can be a single σ -bond or at least one atom with (1) non-bonding electrons (p or other electrons), or (2) π -electrons, or (3) π -electrons and non-bonding electron(s);
- (d) The non-bonding electrons, or π -electrons, or π -electrons and non-bonding electron(s) of the rotor and stators can be localized or de-localized depending on the conformation of the molecule, while the rotor rotates when activated by an E-field;

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(e) The conformation(s) of the molecule can be E-field dependent or bi-stable;

(f) The bi-stable state(s) can be achieved by intra- or inter-molecular forces such as hydrogen bonding, Coulomb force, van der Waals force, metal ion complex or dipole inter-stabilization; and

5 (g) The band gap of the molecule will change depending on the degree of non-bonding electron, or π -electron, or π -electron and non-bonding electron de-localization of the molecule. This will change the electrical properties, such as electrical conductivity, of the molecule.

Following are two examples of this model (Examples 1 and 2):

10 The novel bi-modal molecules of the present invention are active electrical devices that can be switched with an external electric field. The general idea is to design into the molecules a rotatable middle segment (rotor) 32 that has a large dipole moment (see Examples 1 and 2) and that links two other portions of the molecule 30 that are immobilized (stators) 34, as illustrated in FIG. 2. Under the influence of an applied electric field, the vector dipole moment of the rotor 32

15 will attempt to align parallel to the direction of the external field. However, the molecule 30 is designed such that there are inter- and/or intra-molecular forces, such as hydrogen bonding or dipole-dipole interactions as well as steric repulsions, that stabilize the rotor 32 in particular orientations with respect to the stators 34. Thus, a large electric field is required to cause the rotor 32 to unlatch from its initial orientation and rotate with respect to the stators 34.

20 Once switched into a particular orientation, the molecule 30 will remain in that orientation until it is switched to a different orientation, or reconfigured. However, a key component of the molecule design is that there is a steric repulsion or hindrance that will prevent the rotor 32 from rotating through a complete 180 degree half cycle. Instead, the rotation is halted by the steric interaction of bulky groups on the rotor 32 and stators 34 at an electrically significant angle of typically between 10° and 170° from the initial orientation. For the purposes of illustration, this angle

25 is shown as 90° in the present application. Furthermore, this switching orientation may be stabilized by a different set of inter- and/or intra-molecular hydrogen bonds or dipole interactions, and is thus latched in place even after the applied field is turned off. For bi-stable switch molecules, this ability to latch the rotor 32 between two states separated by an electrically significant rotation

30 from the stators is crucial.

When the rotor 32 and stators 34 are all co-planar, the molecule is referred to as "more-conjugated". Thus, the non-bonding electrons, or π -electrons, or π -electrons and non-bonding electrons of the molecule, through its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are delocalized over a large portion of the molecule 30. This

35 is referred to as a "more conductive state" for the molecule, or "electrical state I". In the case where the rotor 32 is rotated out of conjugation by approximately 10° to 170° with respect to the

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stators 34, the conjugation of the molecule 30 is broken and the HOMO and LUMO are localized over smaller portions of the molecule, referred to as "less-conjugated". This is a "less conductive state" of the molecule 30, or "electrical state II". Thus, the molecule 30 is reversibly switchable between two different electrical states.

5 It will be appreciated by those skilled in the art that in the ideal case, when the rotor 32 and stators 34 are completely coplanar, then the molecule is fully conjugated, and when the rotor 32 is rotated at an angle of 90° with respect to the stators 34, then the molecule is non-conjugated. However, due to thermal fluctuations, these ideal states are not fully realized, and the molecule is thus referred to as being "more-conjugated" in the former case and "less-conjugated" in the latter case.

10 Examples 1 and 2 show two different orientations for switching the molecules. In Example 1, the rotation axis of the rotor is designed to be nearly perpendicular to the net current-carrying axis of the molecules, whereas in Example 2, the rotation axis is parallel to the orientation axis of the molecule. These designs allow different geometries of molecular films and electrodes to be used, depending on the desired results. Both generic and real molecular structures are presented
15 for each example. Examples 1a and 2a are generic molecular structures to show two different orientations for switching the molecules, and Examples 1b and 2b are two real molecular structures.

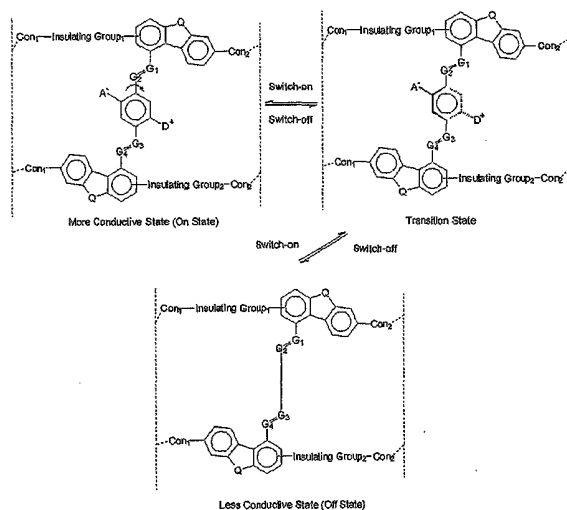
Turning first to Example 1, this depicts a first embodiment of the bi-stable molecular mechanical device of the present invention. Example 1a below depicts a generic molecular implementation for the stator-rotor-stator model.

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Example 1a

5 where:

The letter A⁻ represents an Acceptor group; it is an electron-withdrawing group. It may be one of following: hydrogen, carboxylic acid or its derivatives, sulfuric acid or its derivatives, phosphoric acid or its derivatives, nitro, nitrile, hetero atoms (e.g., N, O, S, P, F, Cl, Br), or functional group with at least one of above-mentioned hetero atoms (e.g., OH, SH, NH, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

10

The letter D⁺ represents a Donor group; it is an electron-donating group. It may be one of following: hydrogen, amine, OH, SH, ether, hydrocarbon (either saturated or unsaturated), or substituted hydrocarbon or functional group with at least one of hetero atom (e.g., B, Si, N, O, S, P, I). The donor is differentiated from the acceptor by that fact that it is less electronegative, or more electropositive, than the acceptor group on the molecule.

15

The letters Con₁ and Con₂ represent connecting units between a molecule and the solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (utilizing a hydrogen bond), multivalent hetero atoms (i.e., C, N, O, S, P, etc.)

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or functional groups containing these hetero atoms (e.g., NH, PH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

The letters G₁, G₂, G₃, and G₄ are bridging groups. The function of these bridging groups is to connect the stator and rotor or to connect two or more conjugated rings to achieve a desired electronic property. They may be any one of the following: hetero atoms (e.g., N, O, S, P, etc.) or functional groups with at least one of above-mentioned hetero atoms (e.g., NH or NHNH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons. The connector may alternately comprise a single atom bridge such as an ether bridge with an oxygen atom, or a direct sigma bond between the rotor and stator.

The letter Q is used here to designate a connecting unit between two phenyl rings. It can be any one of following: S, O, NH, NR, hydrocarbon, or substituted hydrocarbon.

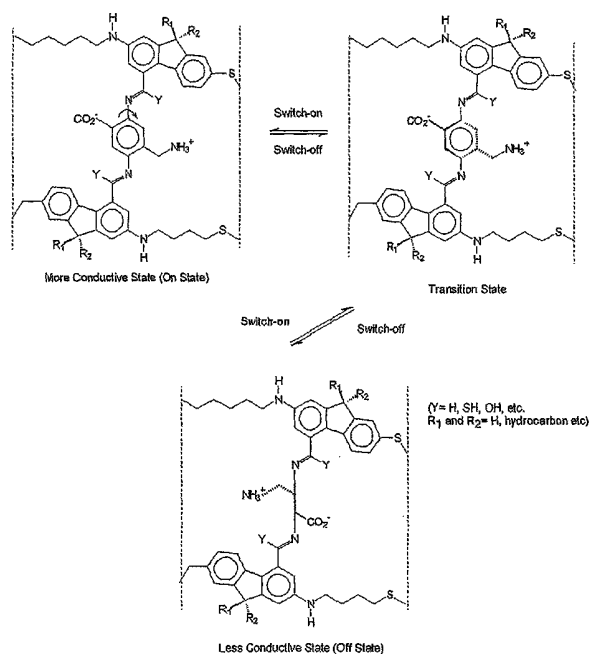
In Example 1a above, the vertical dotted lines represent other molecules or solid substrates. The direction of the switching field is perpendicular to the vertical dotted lines. Such a configuration is employed for electrical switching, and the molecule may be simply placed between the two electrodes.

Example 1b below is a real molecular example of the stator-rotor-stator model mentioned above:

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Example 1b

- 5 The molecule shown above (Example 1b) has been designed with the internal rotor 32 perpendicular to the orientation or current-flow axis of the entire molecule 30. In this case, the external field is applied along the orientation axis of the molecule 30 as pictured - the electrodes (vertical dotted lines) are oriented perpendicular to the plane of the paper and perpendicular to the orientation axis of the molecule 30. Application of an electric field oriented from left to right in
- 10 the diagrams will cause the rotor 32 as pictured in the upper left diagram to rotate to the position shown on the lower diagram, and vice versa. In this case, the rotor 32 as pictured in the lower diagram is not coplanar with the rest of the molecule, so this is the OFF or low conductivity state of the molecule, whereas the rotor is substantially coplanar with the rest of the molecule on the

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upper left diagram, so this is the ON or high conductivity state of the molecule. The structure shown in the upper right diagram depicts the transition state of rotation between the upper left diagram (co-planar, conjugated) and the lower diagram (central portion rotated, non-conjugated).

5 The molecule depicted in Example 1 is non-conductive (or comparatively low conductive) in the non-conjugated state. In the conjugated state, the molecule is conductive.

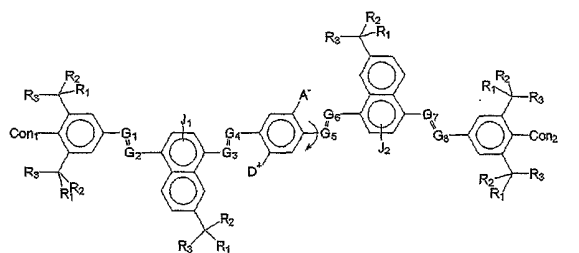
For molecules of the type shown in Example 1, a single monolayer molecular film is grown, for example using Langmuir-Blodgett techniques or self-assembled monolayers, such that the orientation axis of the molecules is perpendicular to the plane of the electrodes used to switch the molecules. Electrodes may be deposited in the manner described by Collier et al, supra, or
10 methods described in the above-referenced patent applications and issued patent.

Turning now to Example 2, this depicts a second embodiment of the bi-stable molecular mechanical device of the present invention. Example 2a below depicts a second generic molecular example for stator-rotor-stator configuration of the present invention.

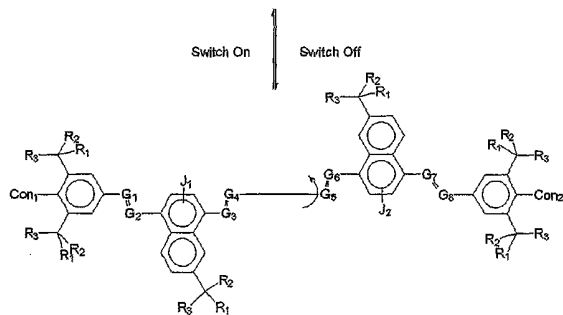
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On State (More Conductive State)



Off State (Less Conductive State)

Example 2a

where:

- 5 The letter A⁻ represents an Acceptor group; it is an electron-withdrawing group. It may be one of following: hydrogen, carboxylic acid or its derivatives, sulfuric acid or its derivatives, phosphoric acid or its derivatives, nitro, nitrile, hetero atoms (e.g., N, O, S, P, F, Cl, Br), or functional group with at least one of above-mentioned hetero atoms (e.g., OH, SH, NH, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.
- 10 The letter D⁺ represents a Donor group; it is an electron-donating group. It may be one of following: hydrogen, amine, OH, SH, ether, hydrocarbon (either saturated or unsaturated), or substituted hydrocarbon or functional group with at least one of hetero atom (e.g., B, Si, I, N, O, S, P).

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The donor is differentiated from the acceptor by that fact that it is less electronegative, or more electropositive, than the acceptor group on the molecule.

The letters Con₁ and Con₂ represent connecting units between one molecule and another molecule or between a molecule and the solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (utilizing a hydrogen bond), multivalent hetero atoms (i.e., C, N, O, S, P, etc.) or functional groups containing these hetero atoms (e.g., NH, PH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

The letters R₁, R₂ and R₃ represent spacing groups built into the molecule. The function of these spacer units is to provide an appropriate 3-dimensional scaffolding to allow the molecules to pack together while providing rotational space for each rotor. They may be any one of the following: hydrogen, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

The letters G₁, G₂, G₃, G₄, G₅, G₆, G₇, and G₈ are bridging groups. The function of these bridging groups is to connect the stator and rotor or to connect two or more conjugated rings to achieve a desired electronic property. They may be any one of the following: hetero atoms (e.g., C, N, O, S, P, etc.) or functional group with at least one of above-mentioned hetero atoms (e.g., NH or NHH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons. The connector may alternately comprise a single atom bridge such as an ether bridge with an oxygen atom, or a direct sigma bond between the rotor and stator.

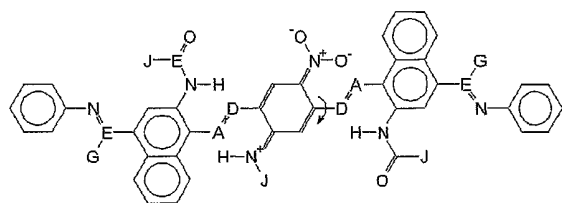
The letters J₁ and J₂ represent tuning groups built into the molecule. The function of these tuning groups (e.g., OH, NHR, COOH, CN, nitro, etc.) is to provide an appropriate functional effect (e.g. both inductive effect and resonance effects) and/or steric effects. The functional effect is to tune the band gap ($\Delta E_{HOMO/LUMO}$) of the molecule to get the desired electronic properties of the molecule. The steric effect is to tune the molecular conformation through steric hindrance, inter- or intramolecular interaction forces (e.g. hydrogen bonding, Coulomb interaction, van der Waals forces) or to provide bi- or multiple-stability of molecular orientations. They may be any one of the following: hydrogen, hetero atoms (e.g., N, O, S, P, B, F, Cl, Br, and I), functional groups with at least one of above-mentioned hetero atoms, hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

Example 2b below is a real molecular example of the stator-rotor-stator configuration mentioned above:

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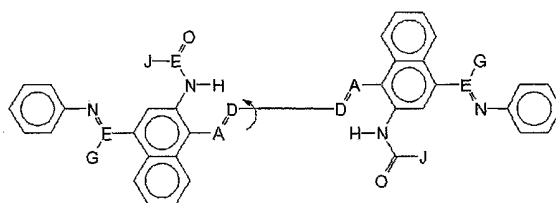
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More Conductive State (On State)

Switch on
⇌
Switch off



Less Conductive State (Off State)

Example 2b

- 5 The molecule shown above (Example 2b) has been designed with the internal rotor parallel to the orientation axis of the entire molecule. In this case, the external field is applied perpendicular to the molecular axis - the electrodes are oriented parallel to the long axis of the molecule and can be either perpendicular or parallel to the plane of the above model structures. For example, application of an electric field to the upper molecule shown above where the field lines are perpendicular to the molecular axis and pointing upward will cause the rotor as pictured in that diagram to rotate to approximately 90 degrees and appear edge on, as shown in the lower molecular diagram above, and vice versa. In this case, the rotor as pictured in the lower diagram is not coplanar with the rest of the molecule, so this is the OFF or low conductivity state of the molecule, whereas the rotor is coplanar with the rest of the molecule on the upper diagram, so this is the ON
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or high conductivity state of the molecule. In the diagram, the letters A, D, E, G, and J indicate sites where different chemical units can be utilized to adjust the geometrical structure of the molecule, and other chemical groups may also be used as the rotor and stators. (The letters N, H, and O retain their usual meaning.) The letters A, D, E, G, and J can be any of the following: heteroatoms (e.g., N, O, S, P, etc.), hydrocarbon (either saturated or unsaturated), or hydrocarbon with at least one of the above-mentioned heteroatoms. In addition to the foregoing, the letters G and J can be any of the following heteroatoms: hydrogen, F, Cl, Br, I, etc.

For the molecules of Example 2, the films are grown such that the molecular axis is parallel to the plane of the electrodes. This may involve films that are multiple monolayers thick. The molecules form solid-state or liquid crystals in which the large stator groups are locked into position by intermolecular interactions or direct bonding to a support structure, but the rotor is small enough to move within the lattice of the molecules. With the proper orientation of electrodes, this structure can be used to create a gated junction (transistor); i.e., one where a voltage applied to one electrode can control the current that flows between two other electrodes that are bridged by the molecules.

Although connector units are not shown in Examples 2a and 2b, such connector units, for example, -S-, depicted in Examples 1a and 1b, would be used to connect the molecule between a pair of electrodes, as depicted in Example 1. Specifically, connection is between the stator portions of the molecule and the electrodes.

Examples 1 and 2 show two different orientations for switching the molecules. However, the examples given are not to be considered limiting the invention to the specific molecular systems illustrated, but rather merely exemplary of the switching mechanism disclosed and claimed herein.

Thus, the present invention introduces a new type of switching mechanism that distinguish it from the prior art, namely, an electric field ("E-field") induced rotation of a rotatable section (rotor) of a molecule to change the band gap of the molecule. The molecule is never oxidized nor reduced in the toggling of the switch, in contrast to prior art approaches. Also, the part of the molecule that moves is quite small, so the switching time is expected to be quite fast. Also, the molecules are much simpler and thus easier and cheaper to make than the rotaxanes, catenanes, and related compounds.

The technology disclosed and claimed herein for forming crossed wires (micro-meter or nanometer) may be used to perform a variety of functions and to form a variety of useful devices and circuits for implementing computing on a microscale and even on a nanoscale. For example, applications include molecular wire crossbar interconnects (MWCI) for signal routing and communications, molecular wire crossbar memory (U.S. Patent 6,128,214), molecular wire crossbar logic (MWCL) employing programmable logic arrays, a demultiplexer for a molecular wire crossbar network, molecular wire transistors, and pixel arrays for displays.

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As illustrated in FIG. 3, the switch 10 of the present invention can be replicated in a two-dimensional array to form a plurality, or array, 60 of switches to form a crossbar switch. FIG. 3 depicts a 6x6 array 60, but the invention is not so limited to the particular number of elements, or switches, in the array. Access to a single point, e.g., 2b, is done by impressing voltage on wires 2 and 5 2 to cause a change in the state of the molecular species 18 at the junction thereof, as described above. Thus, access to each junction is readily available for configuring only those pre-selected junctions in accordance with the teachings herein. Details of the operation of the crossbar switch array 60 are further discussed in above-referenced U.S. Patent 6,128,214.

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INDUSTRIAL APPLICABILITY

The field-switchable molecules disclosed herein are expected to find use in micro-scale and nano-scale electronic devices.

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CLAIMSWhat Is Claimed Is:

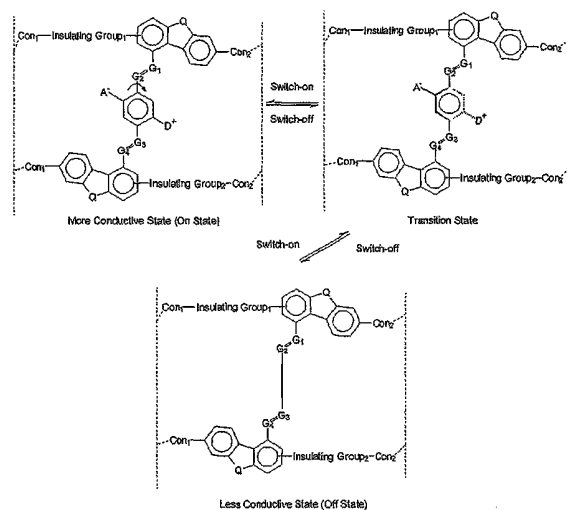
- 5 1. A bi-stable molecular mechanical device (60) comprising a molecular system (30) configured within an electric field generated by a pair of electrodes (12, 14) and electrically connected thereto, said molecular system (30) having one rotor portion (32) connected between two stator portions (34), wherein said rotor portion (32) rotates with respect to said stator portions (34) between at least two different states upon application of said electric field, thereby inducing a band
- 10 gap change in said molecular system (30), wherein in a first state, there is extended conjugation over at least most of said molecular system (30), resulting in a relatively smaller band gap, and wherein in a second state, said extended conjugation is destroyed, resulting in a relatively larger band gap.
- 15 2. The molecular device (60) of Claim 1 wherein said molecular system (30) has an orientation axis and wherein said rotor portion (32) is oriented perpendicular to said orientation axis, with said external electric field applied parallel to said orientation axis.
- 20 3. The molecular device (60) of Claim 2 wherein said molecular system (30) comprises:

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where

A⁺ is an Acceptor group comprising an electron-withdrawing group selected from the group consisting of: (a) hydrogen, (b) carboxylic acid and its derivatives, (c) sulfuric acid and its derivatives, (d) phosphoric acid and its derivatives, (e) nitro, (f) nitrile, (g) hetero atoms selected from the group consisting of N, O, S, P, F, Cl, and Br, (h) functional group with at least one of said hetero atoms, (i) saturated or unsaturated hydrocarbons, and (j) substituted hydrocarbons;

D⁺ is a Donor group comprising an electron-donating group selected from the group consisting of: (a) hydrogen, (b) amines, (c) OH, (d) SH, (e) ethers, (f) saturated or unsaturated hydrocarbons, (h) substituted hydrocarbons, and (i) functional groups with at least one of hetero atom selected from the group consisting of B, Si, N, O, S, P, and I, wherein said Donor group is more electropositive than said Acceptor group;

Con₁ and Con₂ are connecting units between a molecule and a solid substrate selected from the group consisting of a metal electrode, an inorganic substrate, and an organic substrate, said connecting units independently selected from the group consisting of: (a) hydrogen (utilizing a hydrogen bond), (b) multivalent hetero atoms selected from the group consisting of C, N, O, S, and P, (c) functional groups containing said hetero atoms, (d) saturated or unsaturated hydrocarbons, and (d) substituted hydrocarbons;

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G₁, G₂, G₃, and G₄ are bridging groups for connecting said stator to each rotor or to connect two or more conjugated rings to achieve a desired electronic property, said bridging groups selected from the group consisting of: (a) hetero atoms selected from the group consisting of N, O, S, and F, (b) functional groups with at least one of said hetero atoms, (c) saturated or unsaturated hydrocarbons, (d) substituted hydrocarbons, (e) a single atom bridge, and (f) a direct sigma bond between said rotor and each stator; and

Q is a connecting unit between two phenyl rings and is selected from the group consisting of: (a) S, (b) O, (c) NH, (d) NR, (e) hydrocarbon, and (f) substituted hydrocarbon, and where the vertical dashed lines represent said solid substrate to which said molecule is electrically attached.

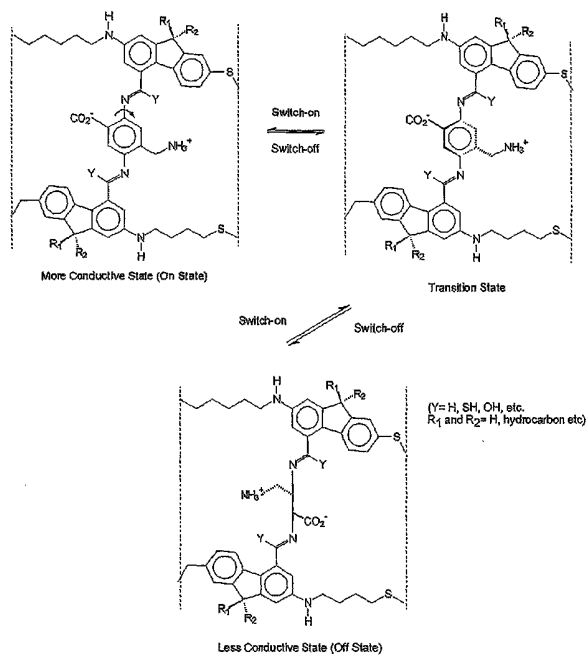
4. The molecular device (60) of Claim 3 wherein said molecular system (30) comprises:

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where:

R₁ and R₂ are independently hydrogen or hydrocarbon; and

Y is selected from the group consisting of hydrogen, OH, and SH.

5 The molecular device (60) of Claim 1 wherein said molecular system (30) has an orientation axis and wherein said rotor portion (32) is oriented parallel to said orientation axis, with said external electric field applied perpendicular to said orientation axis.

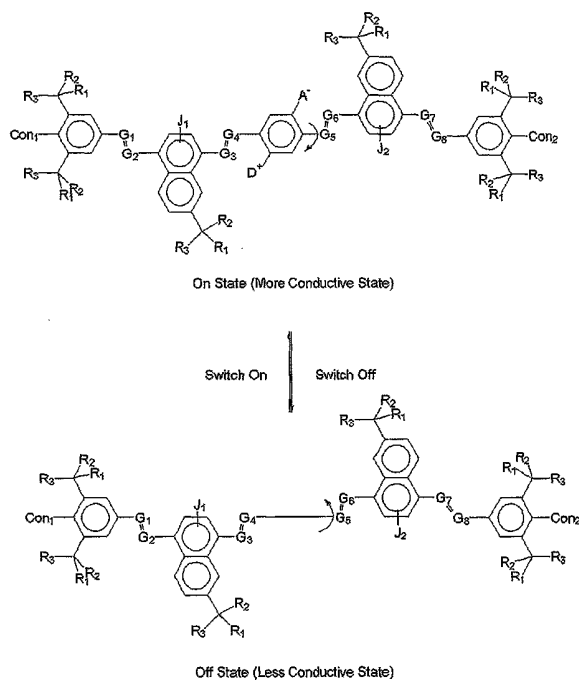
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6 The molecular device (60) of Claim 5 wherein said molecular system (30) comprises:

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where:

- 5 A⁺ is an Acceptor group comprising an electron-withdrawing group selected from the group consisting of: (a) hydrogen, (b) carboxylic acid and its derivatives, (c) sulfuric acid and its derivatives, (d) phosphoric acid and its derivatives, (e) nitro, (f) nitrile, (g) hetero atoms selected from the group consisting of N, O, S, P, F, Cl, and Br, (h) functional groups with at least one of said hetero atoms, (i) saturated or unsaturated hydrocarbons, and (j) substituted hydrocarbons;

- 10 D⁺ is a Donor group comprising an electron-donating group selected from the group consisting of: (a) hydrogen, (b) amines, (c) OH, (d) SH, (e) ethers, (f) saturated and unsaturated hydrocarbons, (g) substituted hydrocarbons, and (i) functional groups with at least one of hetero

atom selected from the group consisting of B, Si, N, O, S, P, and I, wherein said Donor group is more electropositive than said Acceptor group;

Con₁ and Con₂ are connecting units between one molecule and another molecule or between a molecule and a solid substrate selected from the group consisting of a metal electrode, an inorganic substrate, and an organic substrate, said connecting units independently selected from the group consisting of: (a) hydrogen (utilizing a hydrogen bond), (b) multivalent hetero atoms selected from the group consisting of C, N, O, S, and P, (c) functional groups containing said hetero atoms, (d) saturated or unsaturated hydrocarbons, and (e) substituted hydrocarbons;

R₁, R₂ and R₃ are spacing groups for providing an appropriate 3-dimensional scaffolding to allow molecules to pack together while providing rotational space for each rotor, said spacing groups selected from the group consisting of: (a) hydrogen, (b) saturated or unsaturated hydrocarbon, and (c) substituted hydrocarbon;

G₁, G₂, G₃, G₄, G₅, G₆, G₇, and G₈ are bridging groups for connecting said stator to each rotor or to connect two or more conjugated rings to achieve a desired electronic property, said bridging groups selected from the group consisting of: (a) hetero atoms selected from the group consisting of N, O, S, and P, (b) functional groups with at least one of said hetero atoms, (c) saturated or unsaturated hydrocarbons, (d) substituted hydrocarbons, (e) a single atom bridge, and (f) a direct sigma bond between said rotor and each stator; and

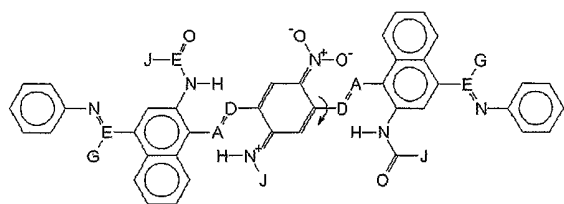
I₁ and I₂ are tuning groups to provide at least one appropriate functional effect selected from the group consisting of inductive effects, resonance effects, and steric effects, said tuning groups being selected from the group consisting of: (a) hydrogen, (b) hetero atoms selected from the group consisting of N, O, S, P, B, F, Cl, Br and I, (c) functional groups with at least one of said hetero atoms, (d) saturated or unsaturated hydrocarbons, and (e) substituted hydrocarbons;

7. The molecular device (60) of Claim 6 wherein said molecular system (30) comprises:

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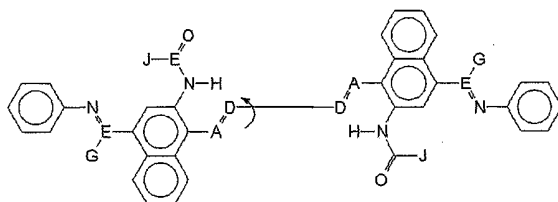
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More Conductive State (On State)

Switch on ⇌ Switch off



Less Conductive State (Off State)

wherein the letters A, D, E, G, and J indicate sites where different chemical units can be utilized to adjust geometrical structure and optical properties of said molecular system and have generic designations as follows: A, D, E, G, and J are independently selected from the group consisting of heteroatoms, hydrocarbons (either saturated or unsaturated), and hydrocarbons with at least one said heteroatom, and where in addition to the foregoing, the letters G and J are independently selected from the group consisting of hydrogen, F, Cl, Br, and I.

8. The molecular device (60) of Claim 1 comprising a crossed-wire device (10) comprising a pair of crossed wires (12, 14) that form a junction (18) where one wire (14) crosses another (12) at an angle other than zero degrees and at least one connector species (16) connecting said pair of crossed wires (12, 14) in said junction (18), said junction (18) having a functional dimension in

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nanometers, wherein said at least one connector species (16) comprises said molecular system (30).

9. The molecular device (60) of Claim 8 wherein said crossed-wire device (10) is selected
5 from the group consisting of memories, logic devices, multiplexers, demultiplexers, configurable interconnects for integrated circuits, field-programmable gate arrays (FPGAs), cross-bar switches, and communication devices.

10. The molecular device (60) of Claim 1 wherein said molecular system (30) is connected to
10 said pair of electrodes (12, 14) by connector units.

11. A bi-stable molecular system (30) comprising the molecular system (30) of Claim 1.

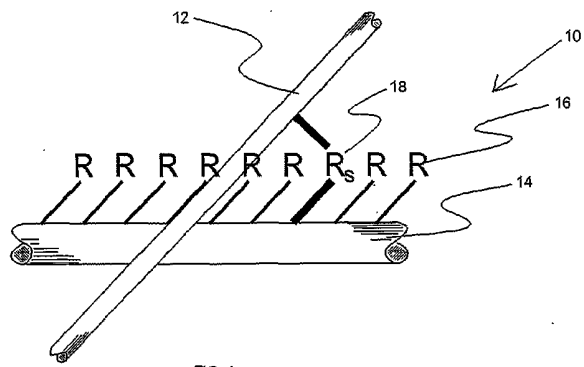


FIG. 1a

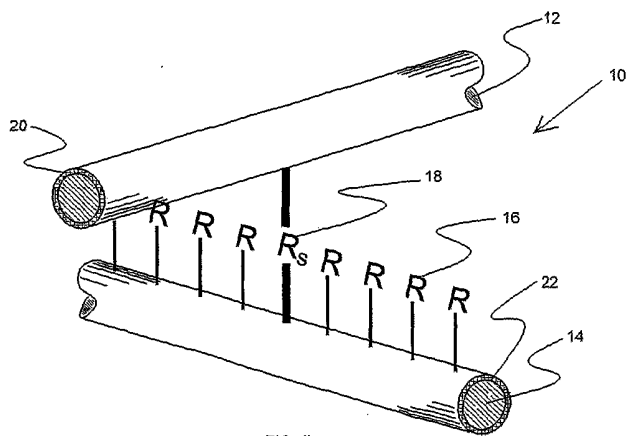


FIG. 1b

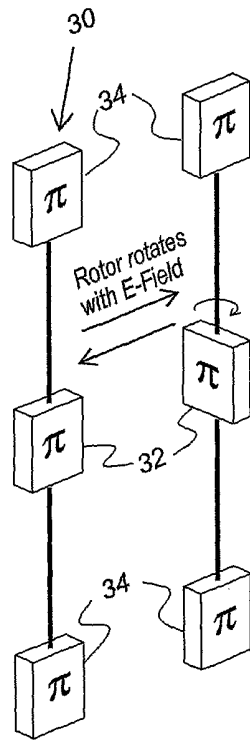


FIG. 2

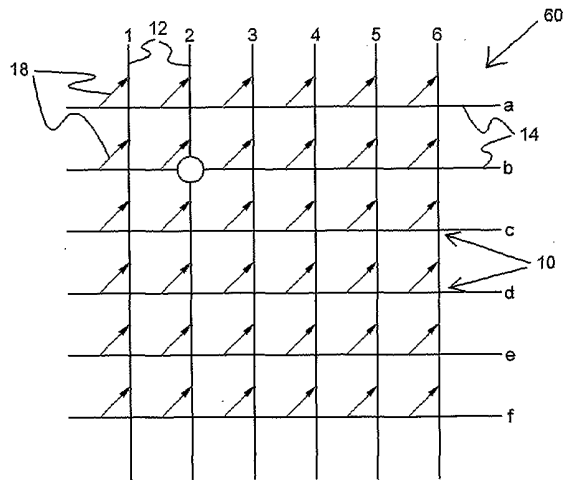


FIG. 3

【国際調査報告】

INTERNATIONAL SEARCH REPORT		International Application No. PCT/US 02/13476
A. CLASSIFICATION OF SUBJECT MATTER IPC 7 H01L51/20		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 128 214 A (HEATH JAMES R ET AL) 3 October 2000 (2000-10-03) cited in the application column 7, line 25 - line 35	1,2,5, 8-11
X	WO 98 35271 A (GIMZENSKI JAMES K ;JUNG THOMAS (CH); SCHLITTLER RAETO R (CH); IBM) 13 August 1998 (1998-08-13) the whole document page 4, line 14 - line 21 page 5, line 27 - line 30 page 6, line 11 - line 13 page 15, line 24 - line 29 --- -/-	1,2,5, 10,11
☒ Further documents are filed in the continuation of box C. ☒ Patent family members are listed in annex.		
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (see specification) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to its international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *Z* document member of the same patent family		
Date of the actual completion of the international search 28 February 2003		Date of mailing of the international search report 06/03/2003
Name and mailing address of the ISA European Patent Office, P.B. 6818 Patentlaan 2 NL - 2000 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax. (+31-70) 340-3016		Authorized officer Bader, K

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INTERNATIONAL SEARCH REPORT		International Application No. PCT/US 02/13476
C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	COLLIER C P ET AL: "Electronically configurable molecular-based logic gates" SCIENCE, AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,, US, vol. 285, no. 5426, 16 July 1999 (1999-07-16), pages 391-394, XP002149479 ISSN: 0036-8075 cited in the application page 391	1,2,5, 10,11

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Information on patent family membersInternational Application No.
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WO 9835271	A	13-08-1998	WO 9835271 A1	13-08-1998
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