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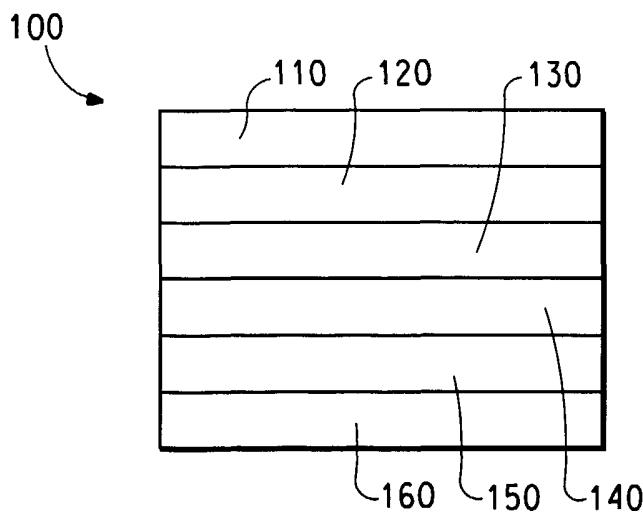
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(54) Title: ELECTRONIC DEVICES MADE WITH ELECTRON TRANSPORT AND/OR ANTI-QUENCHING LAYERS



(57) Abstract: The present invention is directed to a photoactive device comprising an anode, a cathode, and a photoactive layer, which device further comprises an electron transport and/or anti-quenching layer which minimizes both electron transfer quenching and energy transfer quenching of the photoactive layer.

TITLE
ELECTRONIC DEVICES MADE WITH
ELECTRON TRANSPORT AND/OR ANTI-QUENCHING LAYERS
BACKGROUND OF THE INVENTION

5 Cross Reference to Related Applications

This application claims priority from U.S. Provisional Application Serial No. 60/394767, filed July 10, 2002, and U.S. Provisional Application Serial No. 60/458277, filed March 28, 2003.

Field of the Invention

10 The present invention relates to photoactive electronic devices in which there is at least one active layer comprising an electron transport and/or anti-quenching composition.

Description of the Related Art

15 In organic photoactive electronic devices, such as light-emitting diodes ("OLED"), that make up OLED displays, the organic active layer is sandwiched between two electrical contact layers in an OLED display. In an OLED the organic photoactive layer emits light through the light-transmitting electrical contact layer upon application of a voltage across the electrical contact layers.

20 It is well known to use organic electroluminescent compounds as the active component in light-emitting diodes. Simple organic molecules, conjugated polymers, and organometallic complexes have been used.

25 Devices which use photoactive materials, frequently include one or more charge transport layers, which are positioned between the photoactive (e.g., light-emitting) layer and one of the contact layers. A hole transport layer may be positioned between the photoactive layer and the hole-injecting contact layer, also called the anode. An electron transport layer may be positioned between the photoactive layer and the electron-injecting contact layer, also called the cathode.

30 When organometallic compounds, such as Ir and Pt complexes, are used as the electroluminescent layer, a blocking layer inserted next to the luminescent layer on the cathode side can enhance the device efficiency. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (known as BCP or DDPA) was used by Baldo et al. for this purpose. It was proposed that the BCP

35 layer functions as an "exciton blocker" to prevent the transfer of the energy of a luminescent exciton to the adjacent layer. The blocking layer is characterized by a band gap greater than the energy level of excitons formed in the luminescent layer.

US 6,097,147 claims a light emitting device comprising: a substantially transparent anode; a hole transporting layer over said anode; an emission layer over said hole transporting layer; a blocking layer over said emission layer; an electron transporting layer over said blocking layer; 5 and a cathode in electrical contact with said electron transporting layer. It further claims a device wherein said blocking layer is characterized by a band gap greater than the energy level of excitons formed in said emission layer.

However, energy transfer from photoactive materials to an adjacent 10 layer can be quenched not only by energy transfer but also by electron transfer to the adjacent layer, so the use of larger band gap exciton blocker is insufficient. Materials that can prevent both energy transfer quenching and electron transfer quenching are needed.

SUMMARY OF THE INVENTION

15 The present invention is directed to a photoactive device comprising an anode, a cathode, and a photoactive layer, which device further comprises an electron transport and/or anti-quenching layer which minimizes both electron transfer quenching and energy transfer quenching of the photoactive layer.

20 In one embodiment is a photoactive electronic device comprising:

(a) an anode;

(b) a cathode, said cathode having a work function energy level E_3 ;

25 (c) a photoactive layer positioned between said anode and said cathode, said photoactive layer comprising a cyclometallated complex of a transition metal, said cyclometallated complex having a LUMO energy level E_2 and a HOMO energy level E_4 ; and

(d) an electron transport and/or anti-quenching layer positioned between said cathode and said photoactive layer, said electron transport and/or anti-quenching layer having a LUMO energy level E_1 and a HOMO

30 energy level E_5 ,

with the proviso that:

(1) $E_1 - E_3 < 1V$,

(2) $E_1 - E_2 > -1V$, and

(3) $E_4 - E_5 > -1V$.

35 As used herein, the term "charge transport composition" is intended to mean material that can receive a charge from an electrode and facilitates movement through the thickness of the material with relatively high efficiency and small loss of charge. Hole transport compositions are

capable of receiving a positive charge from an anode and transporting it. Electron transport compositions are capable of receiving a negative charge from a cathode and transporting it. The term "anti-quenching composition" is intended to mean a material which prevents, retards, or

5 diminishes both the transfer of energy and the transfer of an electron to/or from the excited state of the photoactive layer to an adjacent layer. The term "photoactive" refers to any material that exhibits electroluminescence, photoluminescence, and/or photosensitivity. The term "HOMO" refers to the highest occupied molecular orbital of a compound. The term "LUMO"

10 refers to the lowest unoccupied molecular orbital of a compound. The term "group" is intended to mean a part of a compound, such as a substituent in an organic compound. The prefix "hetero" indicates that one or more carbon atoms has been replaced with a different atom. The term "alkyl" is intended to mean a group derived from an aliphatic hydrocarbon

15 having one point of attachment, which group may be unsubstituted or substituted. The term "heteroalkyl" is intended to mean a group derived from an aliphatic hydrocarbon having at least one heteroatom and having one point of attachment, which group may be unsubstituted or substituted. The term "alkylene" is intended to mean a group derived from an aliphatic

20 hydrocarbon and having two or more points of attachment. The term "heteroalkylene" is intended to mean a group derived from an aliphatic hydrocarbon having at least one heteroatom and having two or more points of attachment. The term "alkenyl" is intended to mean a group derived from a hydrocarbon having one or more carbon-carbon double

25 bonds and having one point of attachment, which group may be unsubstituted or substituted. The term "alkynyl" is intended to mean a group derived from a hydrocarbon having one or more carbon-carbon triple bonds and having one point of attachment, which group may be unsubstituted or substituted. The term "alkenylene" is intended to mean a

30 group derived from a hydrocarbon having one or more carbon-carbon double bonds and having two or more points of attachment, which group may be unsubstituted or substituted. The term "alkynylene" is intended to mean a group derived from a hydrocarbon having one or more carbon-carbon triple bonds and having two or more points of attachment, which

35 group may be unsubstituted or substituted. The terms "heteroalkenyl", "heteroalkenylene", "heteroalkynyl" and "heteroalkynlene" are intended to mean analogous groups having one or more heteroatoms. The term "aryl" is intended to mean a group derived from an aromatic hydrocarbon having

one point of attachment, which group may be unsubstituted or substituted. The term "heteroaryl" is intended to mean a group derived from an aromatic group having at least one heteroatom and having one point of attachment, which group may be unsubstituted or substituted. The term 5 "arylalkylene" is intended to mean a group derived from an alkyl group having an aryl substituent, which group may be further unsubstituted or substituted. The term "heteroarylalkylene" is intended to mean a group derived from an alkyl group having a heteroaryl substituent, which group may be further unsubstituted or substituted. The term "arylene" is 10 intended to mean a group derived from an aromatic hydrocarbon having two points of attachment, which group may be unsubstituted or substituted. The term "heteroarylene" is intended to mean a group derived from an aromatic group having at least one heteroatom and having two points of attachment, which group may be unsubstituted or substituted. 15 The term "arylenealkylene" is intended to mean a group having both aryl and alkyl groups and having one point of attachment on an aryl group and one point of attachment on an alkyl group. The term "heteroarylenealkylene" is intended to mean a group having both aryl and alkyl groups and having one point of attachment on an aryl group and one 20 point of attachment on an alkyl group, and in which there is at least one heteroatom. Unless otherwise indicated, all groups can be unsubstituted or substituted. The phrase "adjacent to," when used to refer to layers in a device, does not necessarily mean that one layer is immediately next to another layer. On the other hand, the phrase "adjacent R groups," is used 25 to refer to R groups that are next to each other in a chemical formula (i.e., R groups that are on atoms joined by a bond). The term "compound" is intended to mean an electrically uncharged substance made up of molecules that further consist of atoms, wherein the atoms cannot be separated by physical means. The term "ligand" is intended to mean a 30 molecule, ion, or atom that is attached to the coordination sphere of a metallic ion. The term "complex", when used as a noun, is intended to mean a compound having at least one metallic ion and at least one ligand. The term "cyclometallated complex" is intended to mean a complex in which an organic ligand is bound to a metal in at least two positions to 35 form a cyclic metal ligand structure, and in which at least one point of attachment is a metal-carbon bond. In addition, the IUPAC numbering system is used throughout, where the groups from the Periodic Table are

numbered from left to right as 1 through 18 (CRC Handbook of Chemistry and Physics, 81st Edition, 2000).

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Unless otherwise defined, all letter symbols in the figures represent atoms with that atomic abbreviation. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below.

5 All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

10 15 Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of a light-emitting diode (LED).

Figure 2 is a schematic diagram of the energy levels in an LED.

20 Figure 3 shows Formulae I(a) through I(e) for electroluminescent iridium complexes.

Figure 4 shows Formula II for an electron transport composition.

Figure 5 shows Formulae II(a) through II(i) for an electron transport composition.

25 Figure 6 shows Formulae III(a) and III(b) for an electron transport composition.

Figure 7 shows Formulae IV(a) through IV(h) for a multidentate linking group.

Figure 8 shows Formula IV for an electron transport composition.

30 Figure 9 shows Formulae IV(a) through IV(ag) for an electron transport composition.

Figure 10 shows Formula shows Formula VI for an electron transport composition.

Figure 11 shows Formulae VI(a) through VI(m) for an electron transport composition.

35 Figure 12 shows Formula VII for an electron transport composition.

Figure 13 shows formulae for known electron transport compositions.

Figure 14 is a schematic diagram of a testing device for an LED.

Figure 15 is a diagram of EL efficiency for devices using iridium complex I(a).

Figure 16 is a diagram of EL efficiency for devices using iridium complex I(b).

Figure 17 is a plot showing the best ET/AQ compositions for different iridium complex emitters.

Figure 18 is a plot of the LUMO of the iridium complex emitters vs the LUMO of ET/AQ compositions.

10

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to an electronic device comprising at least one electron transport and/or anti-quenching layer and a photoactive layer positioned between two electrodes. The device 100, shown in Figure 1, has an anode layer 110 and a cathode layer 160. Adjacent to the anode is a layer 120 comprising hole transport material. Adjacent to the cathode is a layer 140 comprising an electron transport and/or anti-quenching material. Between the hole transport layer and the electron transport and/or anti-quenching layer is the photoactive layer 130. As an option, devices frequently use another electron transport layer 150, next to the cathode. Layers 120, 130, 140, and 150 are individually and collectively referred to as the active layers.

Depending upon the application of the device 100, the photoactive layer 130 can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector). Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, and phototubes, and photovoltaic cells, as these terms are described in Markus, John, *Electronics and Nucleonics Dictionary*, 470 and 476 (McGraw-Hill, Inc. 1966). A device within the scope of this invention shall mean a light-emitting diode, light-emitting electroluminescent device, or a photodetector as defined above.

Figure 2 shows the schematics of the energetics of the devices, which will be used for the discussion below. All of the energy levels are referenced to the vacuum level, 117, with an energy defined to be zero. As such, they are all negative numbers. The lowest un-occupied molecular orbital (LUMO) energy level of the ET/AQ layer is defined as E_1 . The

LUMO of the photoactive layer is defined as E_2 . The work function of the cathode is defined as E_3 , the highest occupied molecular orbital (HOMO) of the photoactive layer is defined as E_4 , and the HOMO of the ET/AQ layer is defined as E_5 . Higher energy means the energy level is closer to the vacuum level. These energy levels can be measured in the solid state by techniques such as photoelectron spectroscopy. One can also use cyclic voltammetry measurement in solution to measure the relative energy levels of the molecule.

5 An effective electron transport and/or anti-quenching (ET/AQ) material in an electroluminescent device has to possess the following properties.

1. The material has to be able to transport electrons efficiently, preferably with a mobility of $> 10^{-7} \text{ cm}^2/(\text{V}\cdot\text{sec})$.
2. The energy difference between the LUMO of the ET/AQ material and the work function of the cathode has to be small enough to allow efficient electron injection from the cathode. The energy barrier is preferred to be less than 1 V, that is, $E_1-E_3<1 \text{ V}$
3. The LUMO level of ET/AQ has to be high enough to prevent it from receiving an electron from the photoactive layer. This usually requires $E_1-E_2>-1 \text{ V}$. Preferably, $E_1-E_2>0$.
4. The HOMO level of ET/AQ has to be low enough to prevent it from donating an electron to the photoactive layer. This usually requires $E_4-E_5>-1 \text{ V}$. Preferably, $E_4-E_5>0$.

10 Optimal energy level of ET/AQ in criteria 3 and 4 described above can be determined by the application of electron transfer theory. The rate of electron transfer reaction as a function of the energy difference is described by the Marcus theory. (R. A. Marcus, P. Siders, J. Phys. Chem., 86, 622(1982). In its simplest form, it is written as

$$30 \quad k = v \exp [- (E_f - E_i + \lambda)^2 / 4 \lambda k_B T] \quad (1)$$

15 Here, k is the rate constant, k_B the Boltzman constant, T the temperature, E_i and E_f are the energies of the initial and final states, and λ called the reorganization energy, is a phenomenological parameter describing the collective effects of the vibronic interactions in the initial and final states. The pre-factor v involves wave function overlap integrals, α , and is

phenomenologically characterized as depending on the charge separation distance r via

$$v(r) = v_0 \exp [-\alpha(r-r_0)] \quad (2)$$

The prefactor v_0 tends to be universally about 10^{13} sec^{-1} .

10 The energy of the final state, that is, the charge separated state, depends on the separation distance of the electron and hole, r , as well as the applied electric field, E_0 . It can be written as

$$E_f = E_f^\infty - e^2/(\epsilon r) - E_0 z \quad (3)$$

15 where E_f^∞ is the energy of the charge separated state in the absence of an external field and with infinite separation of the electron and hole, ϵ is the dielectric constant of the medium, and z is the direction of the applied field. How to calculate the electron transfer rate under applied field and variable electron hole distance has been discussed before by Wang and Suna,
20 J.Phys.Chem., 101, 5627-5638(1997).

In criteria 3, to prevent significant electron transfer quenching to occur, the LUMO level of the ET/AQ layer has to be high enough such that the electron transfer rate from the photoactive layer to the ET/AQ layer is significantly less than the excited state radiative decay rate of the exciton.
25 So the optimal location of the LUMO level depends on the reorganization energy λ and overlap integral α of the electron transfer reaction involved, and the radiative lifetime of the exciton of the photoactive layer. Typically, this requires $E_1-E_2>-1\text{V}$. Preferably, $E_1-E_2>0$.

In criteria 4, similarly, the HOMO level of the ET/AQ layer has to be low enough such that the electron transfer rate from the ET/AQ layer to the luminescent layer is significantly less than the excited state radiative decay rate of the exciton. The optimal location of the HOMO level depends on the reorganization energy λ and overlap integral α of the electron transfer reaction involved, and the radiative lifetime of the exciton of the photoactive layer. This usually requires $E_4-E_5>-1\text{V}$. Preferably, $E_4-E_5>0$.

For any given photoactive material, there is therefore an optimal ET/AQ material to use which fulfills the requirement outlined in criteria 1 to

4. For a series of structurally similar ET/AQ materials, where the reorganization energy and overlap integral are expected to be similar, one expects to find a correlation between the efficiency of the device and the LUMO energy of the ET/AQ material. For a given photoactive material, 5 there should be an optimal range of the LUMO energies of ET/AQ material where the maximal efficiency is achieved.

It is also to be understood that the ET/AQ material has to be chemically compatible with the photoactive material used. For example, the ET/AQ material has to form a smooth film when deposited on the 10 photoactive material layer. If aggregation occurs, the performance of the device will deteriorate. The occurrence of aggregation can be detected by various known techniques in microscopy and spectroscopy.

The other layers in the device can be made of any materials which are known to be useful in such layers. The anode 110, is an electrode that 15 is particularly efficient for injecting positive charge carriers. It can be made of, for example materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide, or it can be a conducting polymer, and mixtures thereof. Suitable metals include the Group 11 metals, the metals in Groups 4, 5, and 6, and the Group 8-10 transition metals. If the anode 20 is to be light-transmitting, mixed-metal oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, are generally used. The anode 110 may also comprise an organic material such as polyaniline as described in "Flexible light-emitting diodes made from soluble conducting polymer," *Nature* vol. 357, pp 477-479 (11 June 1992). At least one of the anode 25 and cathode should be at least partially transparent to allow the generated light to be observed.

Examples of hole transport materials which may be used for layer 120 have been summarized, for example, in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 18, p. 837-860, 1996, by Y. 30 Wang. Both hole transporting molecules and polymers can be used. The compound bis(4-N,N-diethylamino-2-methylphenyl)-4-methylphenylmethane (MPMP) has been disclosed to be a suitable hole transport composition in Petrov et al., Published PCT application WO 02/02714. Commonly used hole transporting molecules are: 35 N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino) phenyl]cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamine (ETPD), tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-

phenylenediamine (PDA), a-phenyl-4-N,N-diphenylaminostyrene (TPS), p-(diethylamino)benzaldehyde diphenylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), 1-phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl] 5 pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB), N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB), and porphyrinic compounds, such as copper phthalocyanine. Commonly used hole transporting polymers are polyvinylcarbazole, (phenylmethyl)polysilane, and polyaniline and mixtures thereof. It is also 10 possible to obtain hole transporting polymers by doping hole transporting molecules such as those mentioned above into polymers such as polystyrene and polycarbonate.

Examples of the photoactive layer 130 include all known electroluminescent materials. Organometallic electroluminescent 15 compounds are preferred. The most preferred compounds include cyclometalated iridium and platinum electroluminescent compounds and mixtures thereof. Complexes of Iridium with phenylpyridine, phenylquinoline, or phenylpyrimidine ligands have been disclosed as electroluminescent compounds in Petrov et al., Published PCT Application 20 WO 02/02714. Other organometallic complexes have been described in, for example, published applications US 2001/0019782, EP 1191612, WO 02/15645, and EP 1191614. Electroluminescent devices with an active layer of polyvinyl carbazole (PVK) doped with metallic complexes of iridium have been described by Burrows and Thompson in published PCT 25 applications WO 00/70655 and WO 01/41512. Electroluminescent emissive layers comprising a charge carrying host material and a phosphorescent platinum complex have been described by Thompson et al., in U.S. Patent 6,303,238, Bradley et al., in Synth. Met. (2001), 116 (1-3), 379-383, and Campbell et al., in Phys. Rev. B, Vol. 65 085210. as have 30 been Examples of a few suitable iridium complexes are given in Figure 3, as Formulae I(a) through I(e). Analogous tetradeятate platinum complexes can also be used. These electroluminescent complexes can be used alone, or doped into charge-carrying hosts, as noted above.

One type of ET/AQ material is a phenanthroline derivative. The 35 phenanthroline derivative can have Formula II, shown in Figure 4, wherein:

R¹ and R² are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d; a, b, c, and d are 0 or an integer such that a+b = 2n + 1, and c + d = 5,

n is an integer;

x is 0 or an integer from 1 through 3;

y is 0, 1 or 2;

with the proviso that there is at least one substituent on an aromatic group selected from F, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d. Specific examples of such phenanthrolines are Formulae II(a) through II(i) in Figure 5.

The phenanthroline derivative can have Formulae III(a) or II(b), shown in Figure 6, wherein:

R¹, R², a through d, n and x are as defined above;

R³ is the same or different at each occurrence and is selected from a single bond and a group selected from alkylene, heteroalkylene, arylene, heteroarylene, arylenealkylene, and heteroarylenealkylene;

Q is selected from a single bond and a multivalent group;

m is an integer equal to at least 2; and

p is 0 or 1.

Examples of multivalent Q groups are shown as Formulae IV(a) through IV(h) in Figure 7.

Another type of ET/AQ material is a quinoxaline derivative. The quinoxaline derivative can have Formula V, shown in Figure 8, wherein:

R⁴ and R⁵ are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl, alkenylheteroaryl, alkynylheteroaryl, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d, or both of R⁵ together may constitute an arylene or heteroarylene group;

a, b, c, and d are 0 or an integer such that a+b = 2n + 1, and c + d = 5,

n is an integer, and

w is 0 or an integer from 1 through 4.

Specific examples of quinoxalines of this formula are given as Formulae V(a) through V(ag) in Figure 9.

The quinoxaline can have Formula VI, shown in Figure 10, wherein:

R⁴, R⁵, a through d, and n are as defined above,

5 R³ is the same or different at each occurrence and is selected from a single bond and a group selected from alkylene, heteroalkylene, arylene, heteroarylene, arylenealkylene, and heteroarylenealkylene;

Q is selected from a single bond and a multivalent group;

10 m is an integer equal to at least 2;

p is 0 or 1; and

w is 0 or an integer from 1 through 4.

Examples of Q groups are discussed above. Specific examples of quinoxalines of this formula are Formulae VI(a) through VI(m), shown in

15 Figure 11.

The quinoxaline can have Formula VII, shown in Figure 12, where R³, R⁴, R⁵, Q, a through d, m, n, p and w are as defined above,

Examples of additional electron transport materials which can be used in layer 150 include metal chelated oxinoid compounds, such as tris(8-hydroxyquinolato)aluminum (Alq₃); and azole compounds such as 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD) and 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole (TAZ), and mixtures thereof.

25 The cathode 160, is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode can be any metal or nonmetal having a lower work function than the anode. Materials for the cathode can be selected from alkali metals of Group 1 (e.g., Li, Cs), the Group 2 (alkaline earth) metals, the Group 12 metals, including the rare earth elements and lanthanides, and the actinides. Materials such as 30 aluminum, indium, calcium, barium, samarium and magnesium, as well as combinations, can be used. Li-containing organometallic compounds, LiF, and Li₂O can also be deposited between the organic layer and the cathode layer to lower the operating voltage.

It is known to have other layers in organic electronic devices. For 35 example, there can be a layer (not shown) between the anode 110 and hole transport layer 120 to facilitate positive charge transport and/or band-gap matching of the layers, or to function as a protective layer. Layers that are known in the art can be used. In addition, any of the above-

described layers can be made of two or more layers. Alternatively, some or all of anode layer 110, the hole transport layer 120, the electron transport layers 140 and 150, and cathode layer 160, may be surface treated to increase charge carrier transport efficiency. The choice of 5 materials for each of the component layers is preferably determined by balancing the goals of providing a device with high device efficiency.

It is understood that each functional layer may be made up of more than one layer.

The device can be prepared by a variety of techniques, including 10 sequentially vapor depositing the individual layers on a suitable substrate. Substrates such as glass and polymeric films can be used. Conventional vapor deposition techniques can be used, such as thermal evaporation, chemical vapor deposition, and the like. Alternatively, the organic layers 15 can be coated from solutions or dispersions in suitable solvents, using any conventional coating or printing technique, including but not limited to spin-coating, dip-coating, roll-to-roll techniques, ink-jet printing, gravure printing, and screen printing. In general, the different layers will have the following range of thicknesses: anode 110, 500-5000Å, preferably 1000-2000Å; hole transport layer 120, 50-2000Å, preferably 200-1000Å; 20 photoactive layer 130, 10-2000 Å, preferably 100-1000Å; electron transport layer 140 and 150, 50-2000Å, preferably 100-1000Å; cathode 160, 200-10000Å, preferably 300-5000Å. The location of the electron-hole 25 recombination zone in the device, and thus the emission spectrum of the device, can be affected by the relative thickness of each layer. Thus the thickness of the electron-transport layer should be chosen so that the electron-hole recombination zone is in the light-emitting layer. The desired ratio of layer thicknesses will depend on the exact nature of the materials used.

EXAMPLES

30 The following examples illustrate certain features and advantages of the present invention. They are intended to be illustrative of the invention, but not limiting. All percentages are by weight, unless otherwise indicated.

EXAMPLES 1-17

35 These examples illustrate the preparation of some ET/AQ compositions.

EXAMPLE 1

This example illustrates the preparation of Compound V(b) in Figure 9.

5 A mixture of 3,4-diaminotoluene (28.78 g, .236 mol) and benzil (45 g, .214 mol) was refluxed in 738 ml chloroform with 2.16 ml trifluoroacetic acid for 3 hours. The mixture was washed 3 times with 10%HCl, brine, and dried over MgSO₄, filtered, and then filtered through a silica bed with vacuum. The resultant solution was evaporated to dryness. Recrystallized 69 grams of crude product from 550 ml methanol. Filtered solids were 10 dried in a vacuum oven at 50°C for 1 hour to yield 55.56 g of dried solid. 78.8% yield

EXAMPLE 2

This example illustrates the preparation of Compound V(e) in Figure 9.

15 A mixture of 3,4-diaminotoluene (4.49 g, .037 mol) and 4,4'-dimethoxybenzil (9.46g, .035 mol) was refluxed in 125 ml chloroform with 0.35 ml trifluoroacetic acid for 6 hours. The mixture was washed 2 times with water, dried over MgSO₄, and evaporated to ~11 grams. The solid was dissolved in 1:1 ethyl acetate : chloroform for flash chromatography 20 and eluted with ethyl acetate. Evaporated to 9.7 grams of dark solid. 72% yield

EXAMPLE 3

This example illustrates the preparation of Compound V(d) in Figure 9.

25 A mixture of 3,4-diaminotoluene (5.36 g, 44 mmol) and phenanthrene quinone (8.33g, .040 mol) was refluxed in 119 ml chloroform with 0.4 ml trifluoroacetic acid for 6 hours. The mixture was filtered through a medium frit and recrystallized from 430 g of methyl ethyl ketone to yield 5.5 g fluffy wool-like, yellow product. 46% yield

30 EXAMPLE 4

This example illustrates the preparation of Compound V(f) in Figure 10.

35 A mixture of 3,4-diaminotoluene (5.36 g, 44 mmol) and 2,2'-Pyridil (8.49 g, 40 mmol) was refluxed in 119 ml chloroform with 0.4 ml trifluoroacetic acid for 4 hours. The reaction mixture was separated and washed 4 times with 100 ml water, and evaporated to 10.4 grams. The resultant solid was dissolved in 1:1 ethyl acetate:chloroform for flash

chromatography and eluted with ethyl acetate. Evaporated to yield 9.3 grams of solid.

EXAMPLE 5

This example illustrates the preparation of Compound V(g) in
5 Figure 10.

A mixture of methyl-3,4-diaminobenzoate (7.28 g, 44 mmol) and
benzil (8.41 g, 40 mmol) was refluxed in 140 ml methylene chloride for 21
hours. The reaction mixture was evaporated to dryness and then dissolved
10 in 520 ml methanol and 150 ml methylene chloride at reflux. The solution
was then partially evaporated to selectively crystallize the desired product

EXAMPLE 6

This example illustrates the preparation of Compound V(k) in Figure
10.

A mixture of Methyl-3,4-diaminobenzoate (6.37 g, .038 mol) and
15 4,4'-dimethoxybenzil (9.46g, .035 mol) was refluxed in 142 ml methylene
chloride with 3 drops trifluoroacetic acid for 5 hours. 10.7g N-
methylpyrrolidinone was added and reflux continued for 26 more hours.
The mixture was washed 3 times with water, dried over MgSO₄, filtered
20 and then precipitated the product be decanting the organic solution into
550 g methanol. After standing overnight , the product was filtered and
dried at 95°C in vacuum to yield 10.39g product.

EXAMPLE 7

This example illustrates the preparation of Compound V(r) in Figure
10.

25 A mixture of Methyl-3,4-diaminobenzoate (6.12 g, .037 mol) and
phenanthrene quinone (7.08g, .034 mol) was refluxed in 119 ml methylene
chloride. 100 grams of N-methylpyrrolidinone was added and the
chlorinated solvent was distilled out. The pot was warmed to 150°C
whereupon a clear solution was obtained and the reaction was tracked by
30 gas chromatography. The product was precipitated by pouring into 410 g
methanol and the solid precipitate filtered off. The product was
recrystallized from toluene then recrystallized again from a combination of
methyl ethyl ketone 1200 g, toluene 150 g, and tetrahydrofuran 1100 g.
Yield was 3.3 grams of pearly golden wool-like material.

35 EXAMPLE 8

This example illustrates the preparation of Compound V(l) in Figure
10.

A mixture of 1,2-phenylenediamine (13.91 g, .129 mol) and 4,4'-

dibromobenzil (45, .116 mol) was refluxed in 558 ml chloroform with 1.0 ml trifluoroacetic acid for 6 hours. The mixture was washed 3 times with 10% HCl, and evaporated to ~51 grams. Recrystallized from 600 ml ethyl acetate with 100ml methanol at reflux. Large crystals formed overnight 5 and were filtered and washed with methanol twice and dried to 29.63g with a 4.9 g second crop from the chilled mother liquor.

EXAMPLE 9

This example illustrates the preparation of Compound V(h) in Figure 10.

10 A mixture of 2,3-diaminotoluene (4.84 g, .040 mol) and benzil (7.56 g, .036 mol) was refluxed in 112 ml methylene chloride for 19 hours. The mixture was washed 4 times with 12% HCl, and dried over MgSO₄ 15 filtered and evaporated to ~9.5 grams of brown solid. The solid was dissolved into 495 g methanol at reflux and then ~300 g solvent was distilled out. Cooling with ice yielded nice crystals. Filtered and washed crystal cake with methanol.

EXAMPLE 10

This example illustrates the preparation of Compound V(i) in Figure 9.

20 A mixture of 2,3-diaminotoluene (5.05 g, .041 mol) and phenanthrenequinone (7.84 g, ..038 mol) were refluxed in 112 ml chloroform for 29 hours. The resultant solution was chromatographed down a silica column with chloroform eluant. Evaporated product from solvent to yield about 10 grams before vacuum oven drying. Material 25 appeared crystalline

EXAMPLE 11

This example illustrates the preparation of Compound V(j) in Figure 9.

30 A mixture of methyl-3,4-diaminobenzoate (7.28 g, .044 mol) and 2,2'-pyridil (8.48 g, .040 mol) was refluxed in 140 ml methylene chloride for 7 hours. The solution was evaporated to 15.7 grams and the solid dissolved in 240 ml methylene chloride and 140 ml methanol at reflux. After addition of 280 ml methanol and evaporation of ~150 ml of the solvent the solution was left to stand overnight. The resulting solid was 35 collected and dried to 9.8 grams. Took 7.7 g material and dissolved in 203 g methanol with 50 g methylene chloride. Distilled off > 50 ml of solvent. Crystals formed overnight. Filtered and dried in vacuum oven.

EXAMPLE 12

This example illustrates the preparation of Compound VI(a) in Figure 9.

A mixture of 3,3-diaminobenzidine (0.4580 g, 2.14 mmol) and 1,10-phenanthroline-5,6-dione (0.9458 g, 4.5 mmol) were heated at 85°C in 10 g n-methylpyrrolidinone with 0.045 ml trifluoroacetic acid for 23 hours. At ambient temperature chloroform was charged to pot and contents were filtered through a fine frit and washed with acetone, and diethylether then dried at 90°C and vacuum.

10 EXAMPLE 13

This example illustrates the preparation of Compound II(c) in Figure 5.

A mixture of 2,9-diodo-1,10-phenanthroline (900 mg, 2.08 mmol, prepared according to: Toyota et al. *Tetrahedron Letters* **1998**, 39, 2697-2700), 3-trifluoromethylbenzeneboronic acid (989 mg, 5.20 mmol, Aldrich Chemical Company, Milwaukee, WI), tetrakis(triphenylphosphine) palladium (481 mg, 0.416 mmol, Aldrich Chemical Company), and sodium carbonate (882 mg, 8.32 mmol) were allowed to reflux in water (20mL)/toluene (50 mL) for 15 h under nitrogen. Then the organic layer was separated, and the aqueous layer extracted with 3 x 25 mL of chloroform. The organic layers were combined, dried with sodium sulfate, and evaporated to dryness. Purification was accomplished by silica gel flash chromatography with hexanes/dichloromethane (1:1, v:v) as the eluent (product R_f = 0.25), to afford the desired product, >95% pure by ^1H NMR, as a pale yellow solid (560 mg, 57%). ^1H NMR (CDCl_3 , 300 MHz, 296 K): δ 8.81 (s, 2H), 8.63 (d, 2H, J = 7.5 Hz), 8.36 (d, 2H, J = 8.4 Hz), 8.19 (d, 2H, J = 8.41 Hz), 7.84 (s, 2H), 7.68-7.77 (m, 6H) ppm. ^{19}F NMR (CDCl_3 , 282 MHz, 296 K) δ -63.25 ppm.

Compounds II(a), II(g), II(h) and II(i) were made using an analogous procedure.

EXAMPLE 14

This example illustrates the preparation of Compound II(b) in Figure 5.

The same procedure was used as in Example 13, with 3,8-dibromo-1,10-phenanthroline (1.5 g, 4.4 mmol, prepared according to: Saitoh et al. *Canadian Journal of Chemistry* **1997**, 75, 1336-1339.), 4-trifluoromethylbenzeneboronic acid (2.11 g, 11.1 mmol, Lancaster Chemical Company, Windham, NH), tetrakis(triphenylphosphine) palladium

(513 mg, 0.444 mmol), and sodium carbonate (1.41 g, 13.3 mmol), water (20 mL), and toluene (100 mL). Purification was achieved via silica gel flash chromatography (dichloromethane/methanol, 9:1, v:v), and then by washing the product with cold methanol, to afford a white solid (520 mg, 5 25%) >95% pure by ^1H NMR. ^1H NMR (CDCl_3 , 300 MHz, 296 K): δ 9.46 (d, 2 H, J = 2.3 Hz), 8.45 (d, 2H, 2.3 Hz), 7.94 (s, 2H), 7.91 (d, 4H, J = 8.3 Hz), 7.82 (d, 4H, J = 8.4 Hz) ppm. ^{19}F NMR (CDCl_3 , 282 MHz, 296 K) δ -63.12 ppm.

EXAMPLE 15

10 This example illustrates the preparation of Compound II(e) in Figure 5.

2,9-Diiodo-1,10-phenanthroline (1.00 g, 2.31 mmol), 4-fluorobenzeneboronic acid (972 mg, 6.96 mmol), bis(diphenylphosphino)butane (92 mg, 0.23 mmol, Aldrich), palladium 15 acetate (52 mg, 0.23 mmol, Aldrich), and potassium fluoride (810 mg, 13.9 mmol, Aldrich) were allowed to reflux in anhydrous dioxane (100 mL) for 15 h, after which time the dioxane was removed under reduced pressure, and the crude residue was subjected to an aqueous work-up as for Example 1. Purification was achieved via silica gel flash chromatography 20 (dichloromethane, 100% product R_f = 0.57), to afford a pale yellow solid (567 mg, 67%), >95% pure by ^1H NMR. ^1H NMR (CDCl_3 , 300 MHz, 296 K): δ 8.43 (dd, 4 H, $J_{\text{HH}} = 10.4$ Hz, $J_{\text{HF}} = 5.5$ Hz), 8.28 (d, 2H, J = 8.4 Hz), 7.77 (s, 2H), 7.26 (dd, 4H, $J_{\text{HH}} = 9.9$ Hz, $J_{\text{HF}} = 5.9$ Hz) ppm. ^{19}F NMR (CDCl_3 , 282 MHz, 296 K) δ -113.0 ppm.

25 EXAMPLE 16

This example illustrates the preparation of Compound II(d) in Figure 5.

The same procedure was used as in Examples 13 and 14, using 30 4,7-dichloro-1,10-phenanthroline (300 mg, 1.20 mmol, prepared according to: *J. Heterocyclic Chemistry* **1983**, 20, 681-6), 3,5-bis(trifluoromethyl)benzeneboronic acid (0.930 mg, 3.60 mmol, Aldrich), bis(diphenylphosphino)butane (154 mg, 0.361 mmol), palladium acetate (81 mg, 0.361 mmol), sodium carbonate (0.510 mg, 9.62 mmol), water (5 mL), and toluene (30 mL), to afford the desired product as a white solid 35 (410 mg, 56%). ^1H NMR (CDCl_3 , 300 MHz, 296 K): δ 9.35 (d, 2H, J = 4.49 Hz), 8.06 (s, 2H), 8.00 (s, 4H), 7.73 (2H, s), 7.66 (d, 2H, J = 4.52 Hz) ppm. ^{19}F NMR (CDCl_3 , 282 MHz, 296 K) δ -63.32 ppm.

EXAMPLE 17

This example illustrates the preparation of Compound II(f) in Figure 5.

The same procedure was used as in Example 15, using 2,9-dichloro-phenanthroline (1.0 g, 4.01 mmol, prepared according to: Yamada et al. *Bulletin of the Chemical Society of Japan* **1990**, 63, 2710-12), 3,5-bistrifluoromethylbenzene-boronic acid (2.59 g, 10.0 mmol), bis(diphenylphosphino)butane (171 mg, 0.401 mmol), palladium acetate (90 mg, 0.401 mmol), and potassium fluoride (1.40 g, 24.1 mmol), and anhydrous dioxane (100 mL). The product was purified by washing the crude material with diethyl ether, to afford the desired product as a white solid (345 mg, 14%). ^1H NMR (CDCl_3 , 300 MHz, 296 K): δ 8.92 (d, 4H, $J_{\text{HF}} = 1.46$ Hz), 8.45 (d, 2H, $J = 8.3$ Hz), 8.25 (d, 2H, $J = 8.5$ Hz), 8.02 (s, 2H), 7.91 (s, 2H) ppm. ^{19}F NMR (CDCl_3 , 282 MHz, 296 K). δ -63.50 ppm.

The properties of the electron transport and/or anti-quenching compositions are summarized in Table 1 below. Known ET/AQ compounds A and B are shown in Figure 13.

TABLE 1
Properties

Compounds	Absorption onset (nm), E1-E5	Absorption maximum (nm)	$E_{1/2}$ vs SCE (volt),	LUMO vs vacuum (eV), E1
Compound II(b)	382	318	-1.56	-3.28
Compound II(a)	376	320	-1.77	-3.07
Compound II(c)	368	342	-1.68	-3.16
Compound II(d)	362	310	-1.54	-3.3
Compound II(e)	372	342	-1.8	-3.04
Compound II(f)	370	342	-1.52	-3.32
Compound V(a)	375	345	-1.5	-3.33
Compound	378	339	-1.6	-3.24

V(b)				
Compound V(c)	400	385	-1.17	-3.67
Compound V(d)	410	397	-1.3	-3.54
Compound V(g)	390	352	-1.29	-3.55
Compound V(a)	--	--	--	--
Compound V(e)	405	369	-1.66	-3.18
Compound V(f)	378	339	-1.53	-3.31
Compound V(k)	420	382	-1.35	-3.49
Compound V(i)	407	394	-1.28	-3.56
Compound V(h)	385	343	-1.59	-3.25
Compound V(r)	417	401	-1.03	-3.81
Compound V(l)	380	347	-1.49	-3.35
Compound V(j)	380	342	-1.22	-3.62
Comp. A DDPA	368	310	-1.85	-2.99
Comp. B DPA	366	316	-1.95	-2.89

EXAMPLE 18

This example illustrates the preparation of an iridium electroluminescent complex, shown as Formula I(a) in Figure 3.

5 Phenylpyridine ligand, 2-(4-fluorophenyl)-5-trifluoromethylpyridine

The general procedure used was described in O. Lohse, P. Thevenin, E. Waldvogel *Synlett*, 1999, 45-48. A mixture of 200 ml of degassed water, 20 g of potassium carbonate, 150 ml of 1,2-dimethoxyethane, 0.5 g of Pd(PPh₃)₄, 0.05 mol of 2-chloro-5-

trifluoromethylpyridine and 0.05 mol of 4-fluorophenylboronic acid was refluxed (80-90°C) for 16-30 h. The resulting reaction mixture was diluted with 300 ml of water and extracted with CH_2Cl_2 (2 x 100 ml). The combined organic layers were dried over MgSO_4 , and the solvent 5 removed by vacuum. The liquid products were purified by fractional vacuum distillation. The solid materials were recrystallized from hexane. The typical purity of isolated materials was >98%.

Iridium complex:

A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 508 mg), 2-(4-fluorophenyl)-5-trifluoromethylpyridine, from above (2.20 g), AgOCOCF_3 (1.01 g), and water (1 mL) was vigorously stirred under a flow of N_2 as the temperature was slowly (30 min) brought up to 185°C (oil bath). After 2 hours at 185-190°C the mixture solidified. The mixture was cooled down to room 10 temperature. The solids were extracted with dichloromethane until the extracts decolorized. The combined dichloromethane solutions were 15 filtered through a short silica column and evaporated. After methanol (50 mL) was added to the residue the flask was kept at -10°C overnight. The yellow precipitate of the tris-cyclometalated complex, compound b, was separated, washed with methanol, and dried under vacuum. Yield: 20 1.07 g (82%). X-Ray quality crystals of the complex were obtained by slowly cooling its warm solution in 1,2-dichloroethane.

Iridium complex I(c) was made using an analogous procedure.

EXAMPLE 19

This example illustrates the preparation of an iridium 25 electroluminescent complex, shown as Formula I(d) in Figure 3.

Ligand, 2-(2-thienyl)-5-(trifluoromethyl)pyridine:

2-thienylboronic acid (Lancaster Synthesis, Inc., 1.00 g, 7.81 30 mmol), 2-chloro-5-trifluoromethylpyridine (Adrich Chemical Co., 1.417 g, 7.81 mmol), tetrakis(triphenylphosphine) palladium(0) (Aldrich, 451 mg, 35 0.391 mmol), potassium carbonate (EM Science, 3.24 g, 23.4 mmol), water (20 mL), and dimethoxyethane (Aldrich, 20 mL) were allowed to stir at reflux for 20 hours under N_2 , after which time the mixture was cooled to room temperature and the organic and aqueous layers were separated. The aqueous layer was extracted with 3 X 50 mL of diethyl ether, and the 35 combined organic fractions were dried with sodium sulfate, filtered, and the filtrate was evaporated to dryness. The crude product was purified by silica gel flash chromatography with CH_2Cl_2 /hexanes (1:1) as the eluent (product $R_f = 0.5$), to afford the product as a white crystalline solid (yield =

5.2 g, 73% isolated yield). ^1H NMR (CDCl_3 , 296 K, 300 MHz): δ = 7.73-7.57 (2H, m), 7.55 (1H, d, J = 8.5 Hz), 7.34 (1H, d, J = 4.8 Hz), 6.88 (1H, d, J = 4.8 Hz) ppm. ^{19}F NMR (CDCl_3 , 296K, 282 MHz) δ = -62.78 ppm.

Intermediate bridged dimer,

5 [IrCl{2-(2-thienyl)-5-(trifluoromethyl)pyridine}2]2:

2-(2-thienyl)-5-(trifluoromethyl)pyridine from above (555 mg, 2.42 mmol), iridium trichloride (Strem Chemicals, 401 mg, 1.13 mmol), 2-ethoxyethanol (Aldrich Chemical Co., 10 mL) and water (1 mL) were allowed to reflux under nitrogen for 15 hours, after which time the reaction 10 was allowed to cool to room temperature. The resulting precipitated product was collected by filtration, washed with hexanes, and dried in *vacuo*, to afford 575 mg (37%) of the product as a red-orange solid. ^1H NMR (CDCl_3 , 296 K, 300 MHz): δ = 9.30 (4H, d, J = 1.5 Hz), 7.80 (4H, dd, J = 2.0 Hz and 8.5 Hz), 7.59 (4H, d, J = 8.5 Hz), 7.21 (8H, d, J = 4.8 Hz), 15 5.81 (d, 4H, J = 4.9 Hz). ^{19}F NMR (CDCl_3 , 296K, 282 MHz) δ = -62.07 ppm.

Iridium complex [Ir{2-(2-thienyl)-5-(trifluoromethyl)pyridine}3]:

[IrCl{2-(2-thienyl)-5-(trifluoromethyl)pyridine}2]2 from above (100 mg, 0.073 mmol), 2-(2-thienyl)-5-(trifluoromethyl)pyridine from Example 1 (201 mg, 0.88 mmol), and silver trifluoroacetate (Aldrich, 40 mg, 0.18 mmol) were combined and allowed to stir at 170-180 °C under nitrogen for 10 min. Then the mixture was allowed to cool to room temperature and it was redissolved in a minimum amount dichloromethane. The solution was passed through a silica gel column with dichloromethane/hexanes (1:1) as the eluting solvent. The first red-orange fraction to come down the column (product R_f = 0.5) was collected and evaporated to dryness. The residue was suspended in hexanes, and the precipitated product was filtered and washed with excess hexanes to remove any residual 2-(2-thienyl)-5-(trifluoromethyl)pyridine, to afford the product as a red-orange solid.

30 Isolated yield 50 mg (39%). ^1H NMR (CDCl_3 , 296 K, 300 MHz): δ = 7.73-7.57 (6H, m), 7.55 (3H, d, J = 8.5 Hz), 7.34 (3H, d, J = 4.8 Hz), 6.88 (3H, d, J = 4.8 Hz). ^{19}F NMR (CDCl_3 , 296K, 282 MHz) δ = -62.78.

EXAMPLE 20

This example illustrates the formation of OLEDs using the charge 35 transport compositions of the invention.

Thin film OLED devices including a hole transport layer (HT layer), electroluminescent layer (EL layer) and at least one electron transport and/or anti-quenching layer (ET/AQ layer) were fabricated by the thermal

evaporation technique. The base vacuum for all of the thin film deposition was in the range of 10^{-6} torr. The deposition chamber was capable of depositing five different films without the need to break up the vacuum.

Patterned indium tin oxide (ITO) coated glass substrates from Thin Film Devices, Inc were used. These ITO's are based on Corning 1737 glass coated with 1400Å ITO coating, with sheet resistance of 30 ohms/square and 80% light transmission. The patterned ITO substrates were then cleaned ultrasonically in aqueous detergent solution. The substrates were then rinsed with distilled water, followed by isopropanol, and then degreased in toluene vapor for ~3 hours.

The cleaned, patterned ITO substrate was then loaded into the vacuum chamber and the chamber was pumped down to 10^{-6} torr. The substrate was then further cleaned using an oxygen plasma for about 5-10 minutes. After cleaning, multiple layers of thin films were then deposited sequentially onto the substrate by thermal evaporation. Finally, patterned metal electrodes of Al or LiF and Al were deposited through a mask. The thickness of the film was measured during deposition using a quartz crystal monitor (Sycon STC-200). All film thickness reported in the Examples are nominal, calculated assuming the density of the material deposited to be one. The completed OLED device was then taken out of the vacuum chamber and characterized immediately without encapsulation.

The OLED samples were characterized by measuring their (1) current-voltage (I-V) curves, (2) electroluminescence radiance versus voltage, and (3) electroluminescence spectra versus voltage. The apparatus used, 200, is shown in Figure 14. The I-V curves of an OLED sample, 220, were measured with a Keithley Source-Measurement Unit Model 237, 280. The electroluminescence radiance (in the unit of Cd/m²) vs. voltage was measured with a Minolta LS-110 luminescence meter, 210, while the voltage was scanned using the Keithley SMU. The electroluminescence spectrum was obtained by collecting light using a pair of lenses, 230, through an electronic shutter, 240, dispersed through a spectrograph, 250, and then measured with a diode array detector, 260. All three measurements were performed at the same time and controlled by a computer, 270. The efficiency of the device at certain voltage is determined by dividing the electroluminescence radiance of the LED by the current density needed to run the device. The unit is in cd/A.

Iridium compounds XII(b) was made according to the procedure in Appl. Phys. Lett., 1999, 75, 4. The different iridium complexes have the properties given below in Table 2.

EL Compound	Properties of the Iridium compounds				
	$E_{1/2}$ vs SCE, volt	HOMO vs vacuum (eV), E4	$E_{1/2}$ vs SCE, volt	Absorption onset (nm); E2-E4	LUMO vs vacuum (eV), E2
I(a)	1.23	-6.07	-1.68	510	-3.64
I(b)	0.72	-5.56	-2.21	511	-3.13
I(c)	1.17	-6.01	-1.62	539.5	-3.71
I(d)	1.05	-5.89	-1.74	571	-3.72

5

A summary of the device layers and thicknesses is given in Table 3. In all cases the anode was ITO, as discussed above, the HT layer was MPMP, and the cathode was Al having a thickness in the range of 600-800 Å. In some cases, a second ET layer 150 was present. This layer 10 comprised either tris(8-hydroxyquinolato)aluminum(III), Alq, or bis(2-methyl-8-quinolinolato)(para-phenyl-phenolato)aluminum(III), BAlq, as indicated.

Comparative examples, a-d, where no ET/AQ layer were used in the devices were also prepared. These comparative examples 15 demonstrate it is necessary to use ET/AQ layer to achieve good device performance.

Comparative example a2 uses benzophenone as the ET/AQ layer, which yields very poor device performance. Benzophenone is white in color and has a band gap larger than that of EL compound I(a), which is 20 yellow in color. This example demonstrates it is not sufficient to use a larger band gap material in the ET/AQ layer to block energy transfer.

Comparative examples a3 and a4 use compound I(c) as the ET/AQ layer, and either AlQ or BAlQ as the second electron transport layer. Relatively good device performance was obtained in spite of the fact that 25 compound I(c) is orange in color which has a band gap smaller than that of compound I(a), which is yellow in color.

TABLE 3

SAMPLE	HT, Å	EL, Å	ET/AQ, Å	ET, Å
Comparative a	523	I(a) 520		
9-1	506	I(a) 430	II(b) 405	
9-2	507	I(b) 407	Comp. A 408	
9-3	507	I(a) 405	Comp. B 407	
9-4	505	I(a) 404	II(a) 305	
9-5	515	I(a) 407	II(c) 409	
9-6	508	I(a) 411	II(h) 416	
9-7	510	I(a) 408	II(i) 412	
9-8	516	I(a) 419	II(d) 406	
9-9	512	I(a) 434	II(g) 415	
9-10	505	I(a) 415	II(e) 432	
9-11	514	I(a) 402	II(f) 431	
9-12	545	I(a) 403	V(a) 430	Alq 430
9-13	508	I(a) 625	V(b) 425	
9-14	509	I(a) 413	V(c) 416	
9-15	578	I(a) 411	V(d) 381	
9-16	549	I(a) 425	V(g) 423	
9-17	533	I(a) 417	VI(a) 411	
9-18	527	I(a) 418	V(e) 418	
9-19	502	I(a) 403	V(f) 106	Alq 303
9-20	505	I(a) 412	V(k) 439	
9-21	514	I(a) 416	V(i) 408	

9-22	513	I(a) 409	V(h) 414	
9-23	515	I(a) 500	V(r) 410	
9-24	516	I(a) 409	V(l) 432	
9-25	504	I(a) 412	V(j) 402	
Comparative a2	507	I(a) 409	Benzophenone 408	
Comparative a3	519	I(a) 411	I(c) 110	Alq 309
Comparative a4	507	I(a) 413	I(c) 105	BAIq 308
Comparative b	531	I(b) 500		
9-26	512	I(b) 410	Comp. A 406	
9-27	523	I(b) 402	Comp. B 416	
Comparative c	510	I(c) 532		
9-28	512	I(c) 415	II(g) 414	
9-29	516	I(c) 401	II(b) 408	
9-30	512	I(c) 413	Comp. B 407	
9-31	545	I(c) 462	Comp. A 111	Alq 319
9-32	506	I(c) 403	II(d) 472	
9-33	503	I(c) 404	Comp. A 406	
Comparative d	511	I(d) 508		
9-34	504	I(d) 411	Comp. B 418	
9-35	511	I(d) 418	II(d) 407	
9-36	512	I(d) 404	II(g) 402	
9-37	509	I(d) 409	II(b) 409	
9-38	516	I(d) 411	II(a) 406	

The devices were tested as described above and the results are given in Table 4 below.

TABLE 4

SAMPLE	PEAK RADIANCE cd/m ²	PEAK EFFICIENCY cd/A	APPROXIMATE PEAK WAVELENGTHS nm
Comparative a	4 at 21 V	0.01	525
9-1	3500 at 19 V	17	525
9-2	3000 at 22 V	10	525
9-3	4500 at 19 V	20	525
9-4	3500 at 20 V	11	525
9-5	1200 at 25 V	6	525
9-6	1900 at 24 V	8	525
9-7	1600 at 28 V	8.5	525
9-8	2200 at 25 V	16	525
9-9	400 at 21 V	11	525
9-10	1000 at 23 V	6	525
9-11	900 at 27 V	8.5	525
9-12	2300 at 20 V	5.4	525
9-13	2700 at 27 V	10	525
9-14	400 at 15 V	10	525
9-15	90 at 22 V	4.4	525
9-16	2000 at 23 V	13	525
9-17	80 at 20 V	0.01	525
9-18	200 at 22 V	1.1	525
9-19	7000 at 15 V	30	525
9-20	1600 at 22 V	11	525

9-21	300 at 19 V	2.6	525
9-22	1200 at 20 V	9.5	525
9-23	220 at 26 V	2.6	525
9-24	100 at 22 V	1.2	525
9-25	180 at 25 V	8.5	525
Comparative a2	16 at 21 V	0.2	525
Comparative a3	3000 at 22 V	7	525
Comparative a4	750 at 22 V	7	525
Comparative b	160 at 20 V	0.1	522
9-26	700 at 24 V	4	522
9-27	130 at 24 V	1.8	522
Comparative c	30 at 15 V	0.1	560
9-28	2400 at 23 V	13	560
9-29	1400 at 20 V	6.5	560
9-30	2200 at 18 V	5.8	560
9-31	510 at 20 V	2.2	560
9-32	1700 at 22 V	10	560
9-33	2000 at 27 V	5	560
Comparative d	0.1 at 20 V	0.015	
9-34	190 at 26 V	1.5	570
9-35	30 at 26 V	1.1	570
9-36	200 at 24 V	2	570
9-37	50 at 25 V	0.8	570
9-38	430 at 25 V	2.5	570

The peak efficiency is the best indication of the value of the electroluminescent compound in a device. It gives a measure of how many electrons have to be input into a device in order to get a certain number of photons out (radiance). It is a fundamentally important number, 5 which reflects the intrinsic efficiency of the light-emitting material. It is also important for practical applications, since higher efficiency means that fewer electrons are needed in order to achieve the same radiance, which in turn means lower power consumption. Higher efficiency devices also tend to have longer lifetimes, since a higher proportion of injected 10 electrons are converted to photons, instead of generating heat or causing an undesirable chemical side reactions.

As can be seen in the comparative examples of Table 4, devices made without the ET/AQ layer have much lower electroluminescence efficiency than devices made with the ET/AQ layer. Also, for a given 15 photoactive material, different device efficiency can be obtained with different ET/AQ materials, although all of these ET/AQ materials have band gap larger than the energy of the luminescent exciton. This shows that to prevent the quenching of the luminescent exciton, it is not sufficient just to block the energy transfer process. The electron transfer process 20 also has to be blocked. This is done via method outlined in criteria 1-4. Therefore to obtain a maximal electroluminescence efficiency, there exists at least one optimal, matched ET/AQ material for each different electroluminescent material as shown in Table 4.

As examples, the dependence of electroluminescence efficiency on 25 the LUMO energies of the ET/AQ compounds are plotted in Figure 15 and Figure 16 for emitters I(c) and I(d), respectively. For each photoactive material, the efficiency is quite sensitive to the ET/AQ compound used and an optimal ET/AQ compound can be found by tuning the ET/AQ LUMO energy. Figure 17 plots the best ET/AQ compound for all the emitters 30 studied here. As can be seen there is a general correlation between the LUMO of the ET/AQ compound and the LUMO of the emitter, within experimental uncertainty. As the emitter LUMO energy decreases, there is a corresponding decrease in the LUMO energy of the best ET/AQ material. Figure 18 plots the LUMO of the best ET/AQ compound (y) vs. 35 the LUMO of the corresponding emitter (x). The data can be roughly fitted with a linear equation of $y=2(\pm 0.1)+0.273 \cdot x$

CLAIMS

What is claimed is:

1. A photoactive electronic device comprising:
 - 5 (a) an anode;
 - (b) a cathode, said cathode having a work function energy level E_3 ;
 - (c) a photoactive layer positioned between said anode and said cathode, said photoactive layer comprising a cyclometalated complex of a transition metal, said cyclometalated complex having a LUMO energy level E_2 and a HOMO energy level E_4 ; and
 - 10 (d) an electron transport and/or anti-quenching layer positioned between said cathode and said photoactive layer, said electron transport and/or anti-quenching layer having a LUMO energy level E_1 and a HOMO energy level E_5 ,
- 15 with the proviso that:
 - (1) $E_1 - E_3 < 1V$,
 - (2) $E_1 - E_2 > -1V$, and
 - (4) $E_4 - E_5 > -1V$.
- 20 2. The device of Claim 1 wherein $E_1 - E_2 > 0$.
3. The device of Claim 1 wherein $E_4 - E_5 > 0$.
4. The device of Claim 1 wherein said electron transport and/or anti-quenching layer has an electron mobility of at least $10^{-7} \text{ cm}^2/(\text{V}\cdot\text{sec})$.
- 25 5. The device of Claim 1 wherein the electron transport and/or anti-quenching layer comprises a phenanthroline derivative.
6. The device of Claim 5 wherein the phenanthroline derivative has Formula II shown in Figure 4, wherein:

R^1 and R^2 are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, 30 aryl, heteroaryl, $C_nH_aF_b$, $OC_nH_aF_b$, $C_6H_cF_d$, and $OC_6H_cF_d$;
 a , b , c , and d are 0 or an integer such that $a+b = 2n + 1$, and $c + d = 5$;
 n is an integer;
 x is 0 or an integer from 1 through 3; and
- 35 y is 0, 1 or 2;
with the proviso that there is at least one substituent on an aromatic group selected from F, $C_nH_aF_b$, $OC_nH_aF_b$, $C_6H_cF_d$, and $OC_6H_cF_d$.

7. The device of Claim 6, wherein n is an integer from 1 through 12.
8. The device of Claim 5 wherein the phenanthroline derivative is selected from Formulae II(a) through II(i) in Figure 5.
- 5 9. The device of Claim 5 wherein the phenanthroline derivative has Formula III(a), shown in Figure 6, wherein:
 - R¹ and R² are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d;
 - 10 R³ is the same or different at each occurrence and is selected from a single bond and a group selected from alkylene, heteroalkylene, arylene, heteroarylene, arylenealkylene, and heteroarylenealkylene;
 - Q is selected from a single bond and a multivalent group;
 - 15 m is an integer equal to at least 2;
 - p is 0 or 1;
 - and
 - x is 0 or an integer from 1 through 3.
10. The device of Claim 9, wherein:
 - m is an integer from 2 through 10;
 - n is an integer from 1 through 12; and
 - with the proviso that when Q is a single bond, p is 0.
- 20 11. The device of Claim 5, wherein the phenanthroline derivative has Formula III(b), shown in Figure 6, wherein:
 - R¹ and R² are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d;
 - 25 R³ is the same or different at each occurrence and is selected from a single bond and a group selected from alkylene, heteroalkylene, arylene, heteroarylene, arylenealkylene, and heteroarylenealkylene;
 - Q is selected from a single bond and a multivalent group;
 - m is an integer equal to at least 2;
 - p is 0 or 1;
 - 30 and
 - x is 0 or an integer from 1 through 3.
- 35 12. The device of Claim 1 wherein the electron transport and/or anti-quenching layer comprises a quinoxaline derivative.

13. The device of Claim 12 wherein the quinoxaline derivative has Formula V, shown in Figure 8, wherein:

R⁴ and R⁵ are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, 5 aryl, heteroaryl, alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl, alkenylheteroaryl, alkynylheteroaryl, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d, or both of R⁵ together may constitute an arylene or heteroarylene group;

10 a, b, c, and d are 0 or an integer such that a+b = 2n + 1, and c + d = 5;

n is an integer; and

w is 0 or an integer from 1 through 4.

14. The device of Claim 13 wherein n is an integer from 1 through 15 12.

15. The device of Claim 12 wherein the quinoxaline derivative is selected from Formulae V(a), V(b), V(d) through V(i) and V(k) through V(ag) in Figure 9.

16. The device of Claim 12, wherein the quinoxaline derivative is 20 selected from Formulae V(c) and V(j) in Figure 9.

17. The device of Claim 12 wherein the quinoxaline derivative has Formula VI, shown in Figure 10, wherein:

R⁴ and R⁵ are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, 25 aryl, heteroaryl, alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl, alkenylheteroaryl, alkynylheteroaryl, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d, or both of R⁵ together may constitute an arylene or heteroarylene group;

30 R³ is the same or different at each occurrence and is selected from a single bond and a group selected from alkylene, heteroalkylene, arylene, heteroarylene, arylenealkylene, and heteroarylenealkylene;

Q is selected from a single bond and a multivalent group;

35 a, b, c, and d are 0 or an integer such that a+b = 2n + 1, and c + d = 5;

m is an integer equal to at least 2;

n is an integer; and

p is 0 or 1.

18. The device of Claim 17, wherein:

m is an integer from 2 through 10;

n is an integer from 1 through 12; and

5 p is 0.

19. The device of Claim 12 wherein the quinoxaline derivative is selected from Formulae VI(b) through VI(g) and VI(i) through VI(k) in Figure 11.

10 20. The device of Claim 12 wherein the quinoxaline derivative is selected from Formulae VI(a), VI(h), VI(l) and VI(m) in Figure 11.

21. The device of Claim 12, wherein the quinoxaline derivative has Formula VI(m) shown in Figure 11.

22. The device of Claim 12 wherein the quinoxaline derivative has Formula VII, shown in Figure 12, wherein:

15 R⁴ and R⁵ are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl, alkenylheteroaryl, alkynylheteroaryl, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d, or both of R⁵ together may constitute an arylene or 20 heteroarylene group;

25 R³ is the same or different at each occurrence and is selected from a single bond and a group selected from alkylene, heteroalkylene, arylene, heteroarylene, arylenealkylene, and heteroarylenealkylene;

Q is selected from a single bond and a multivalent group;

a, b, c, and d are 0 or an integer such that a+b = 2n + 1, and c + d = 5;

m is an integer equal to at least 2;

30 n is an integer; and

p is 0 or 1.

23. The device of Claims 1-22, wherein the device is a light-emitting diode, a light-emitting electrochemical cell, or a photodetector.

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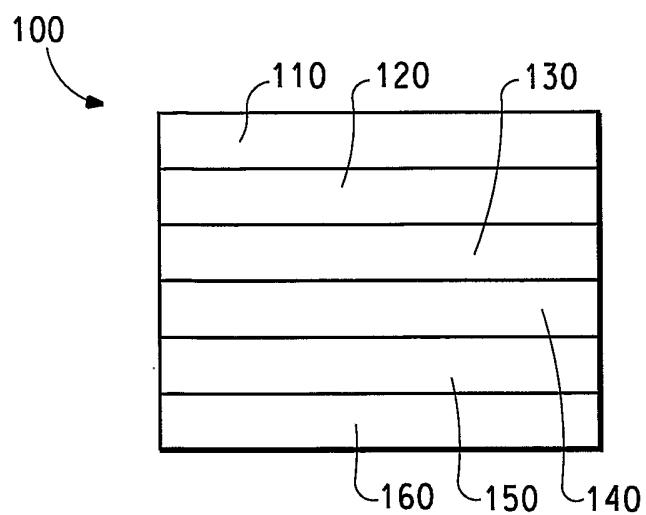


FIG. 1

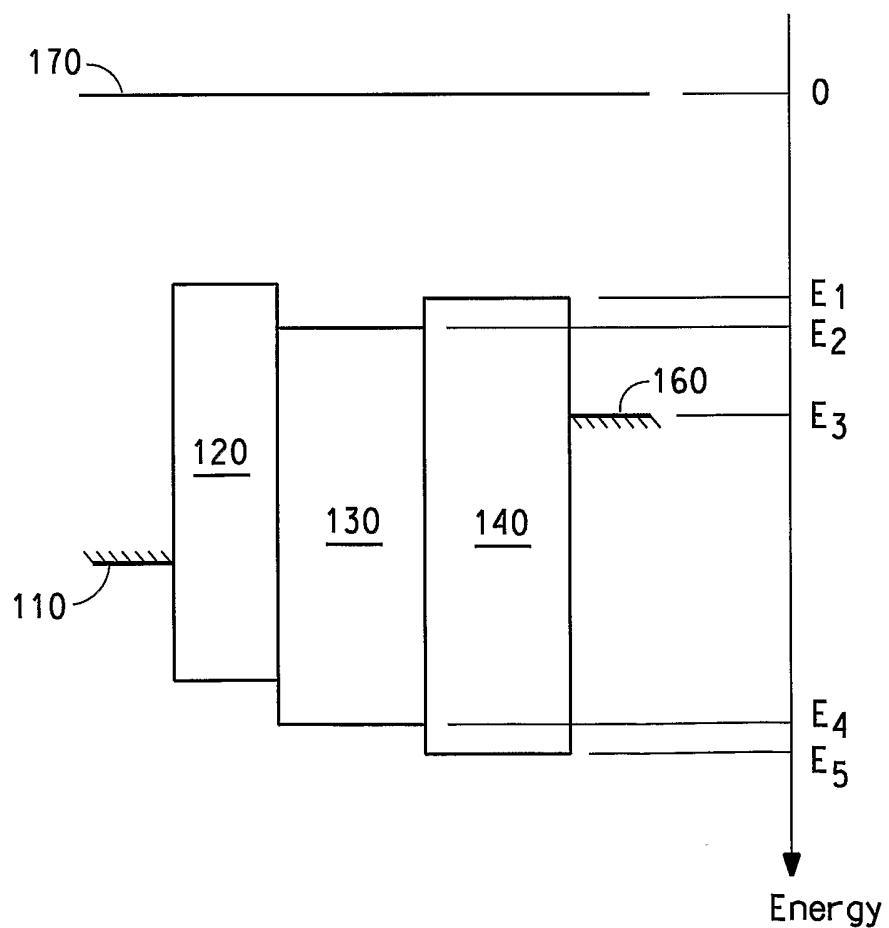
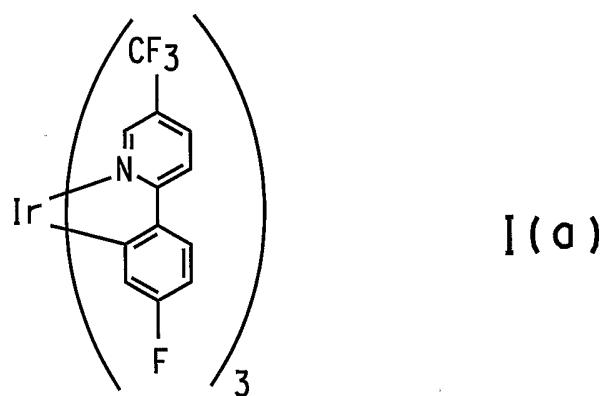


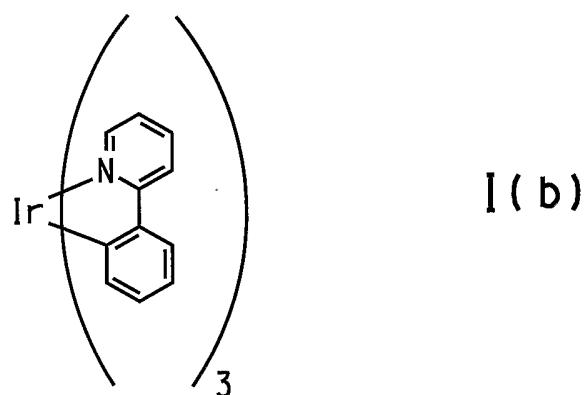
FIG. 2

FIG. 3A



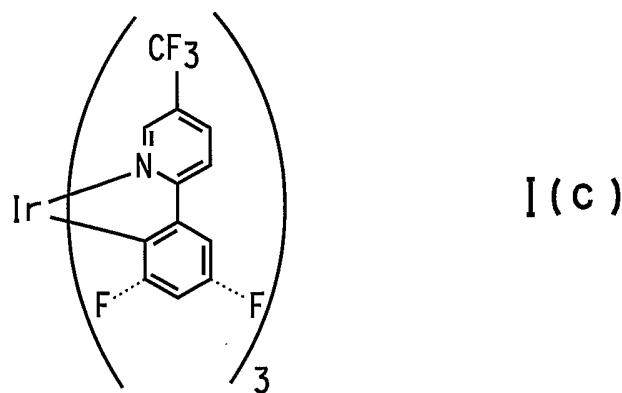
I(a)

FIG. 3B



I(b)

FIG. 3C



I(c)

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FIG. 3D

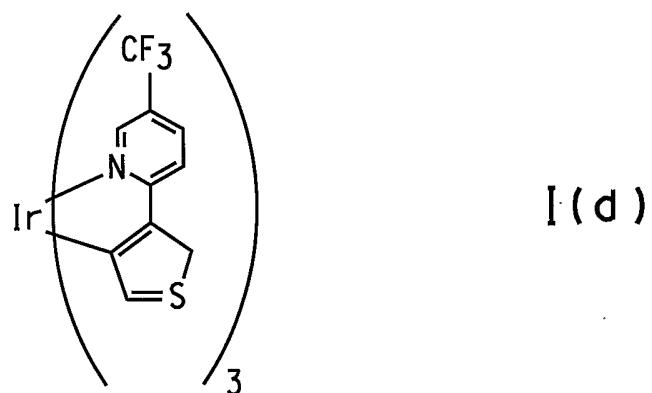


FIG. 3E

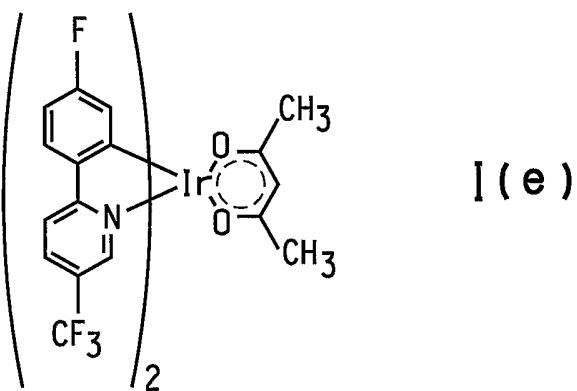


FIG. 4

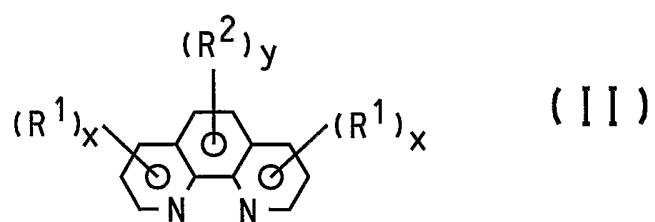
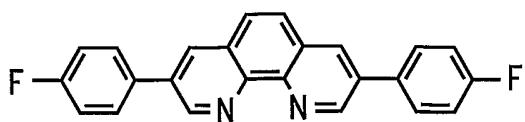
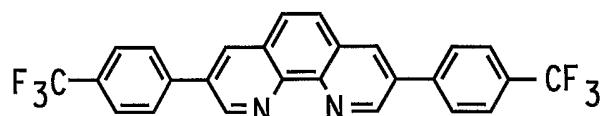


FIG. 5A



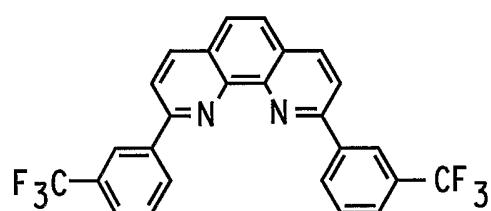
III(a)

FIG. 5B



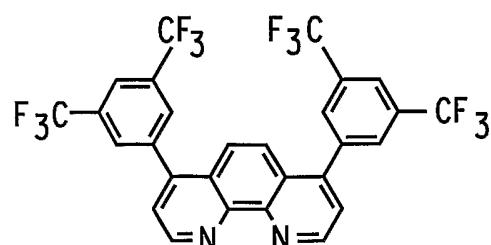
III(b)

FIG. 5C



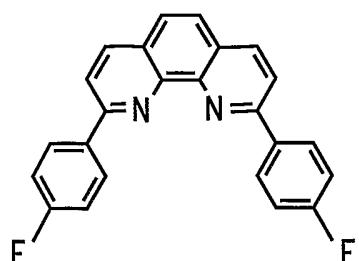
III(c)

FIG. 5D



III(d)

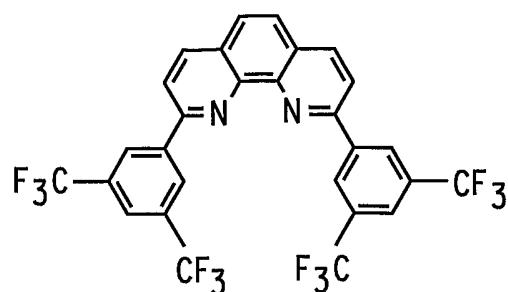
FIG. 5E



III(e)

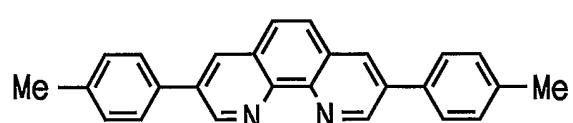
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FIG. 5F



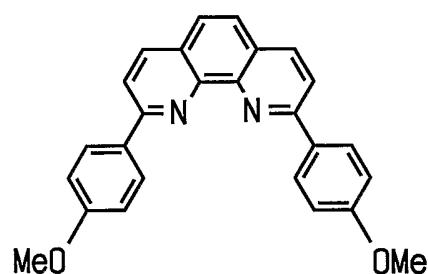
III(f)

FIG. 5G



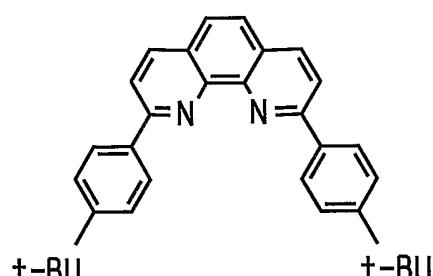
III(g)

FIG. 5H



III(h)

FIG. 5I



III(i)

FIG. 6A

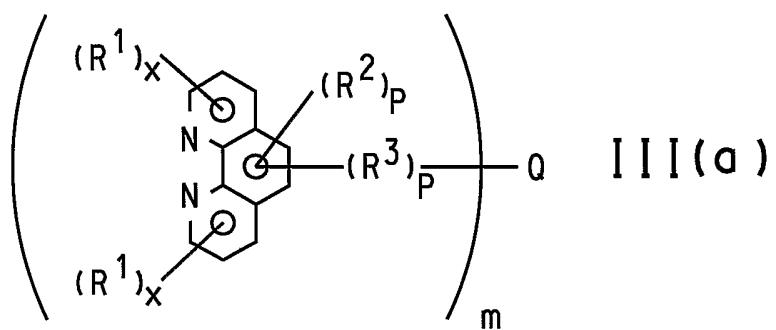
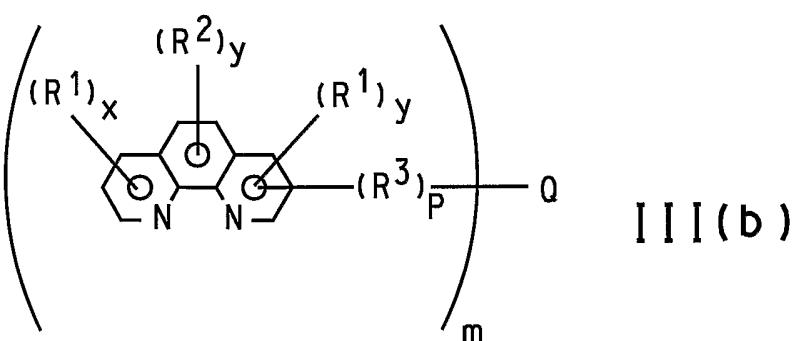
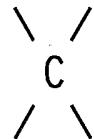


FIG. 6B



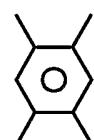
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FIG. 7A



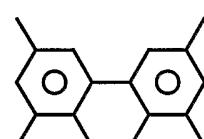
IV(a)

FIG. 7B



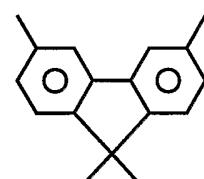
IV(b)

FIG. 7C



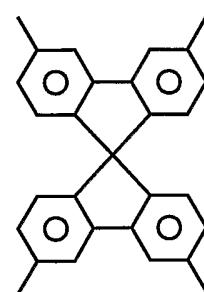
IV(c)

FIG. 7D



IV(d)

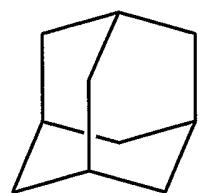
FIG. 7E



IV(e)

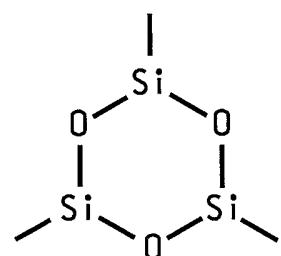
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FIG. 7F



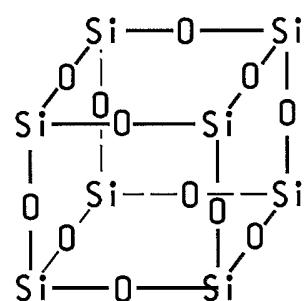
IV(f)

FIG. 7G



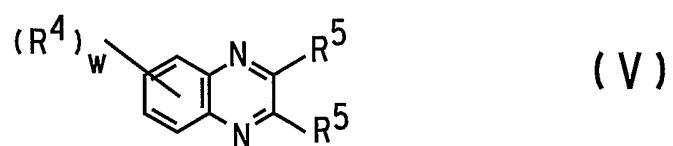
IV(g)

FIG. 7H



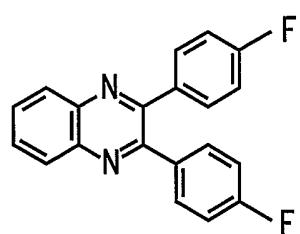
IV(h)

FIG. 8



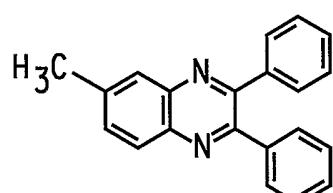
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FIG. 9A



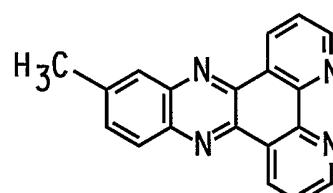
V(a)

FIG. 9B



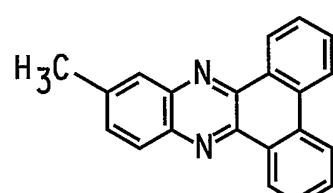
V(b)

FIG. 9C



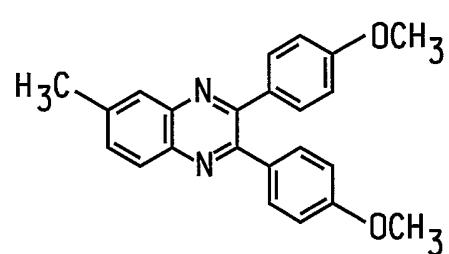
V(c)

FIG. 9D



V(d)

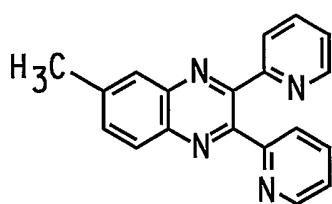
FIG. 9E



V(e)

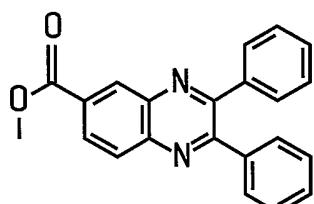
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FIG. 9F



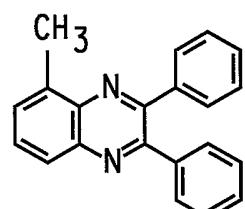
V(f)

FIG. 9G



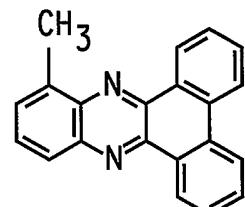
g

FIG. 9H



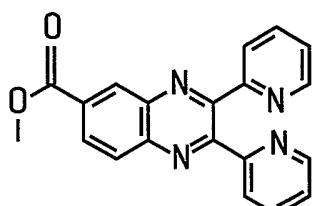
h

FIG. 9I



i

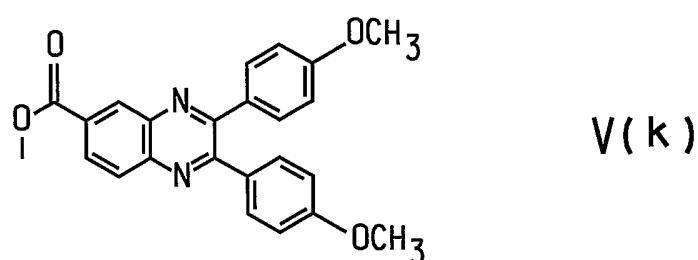
FIG. 9J



j

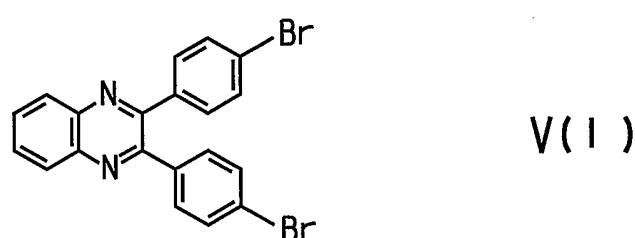
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FIG. 9K



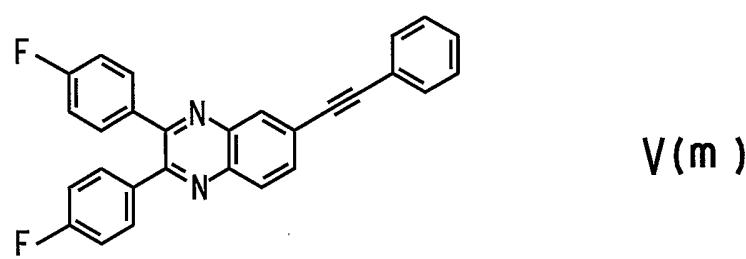
V(k)

FIG. 9L



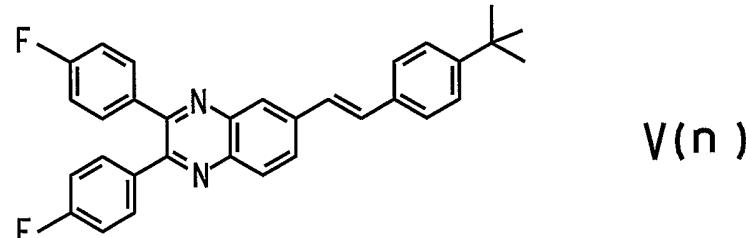
V(l)

FIG. 9M



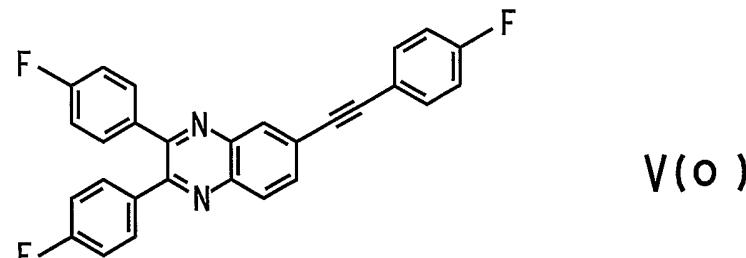
V(m)

FIG. 9N



V(n)

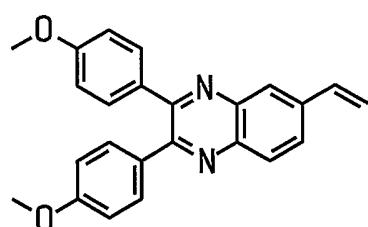
FIG. 9O



V(o)

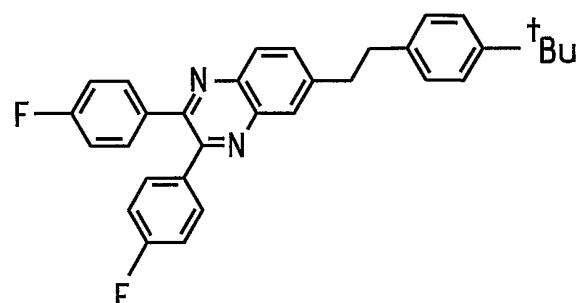
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FIG. 9P



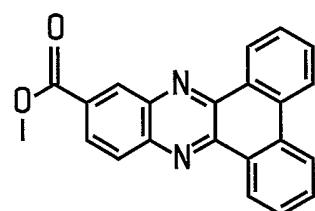
V(p)

FIG. 9Q



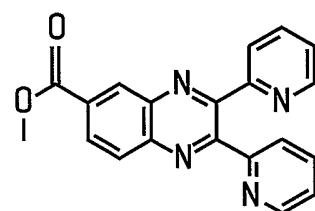
V(q)

FIG. 9R



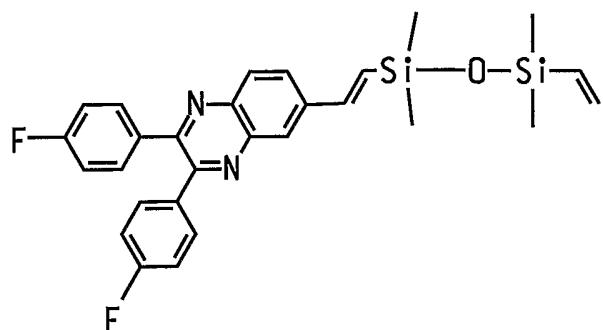
V(r)

FIG. 9S



V(s)

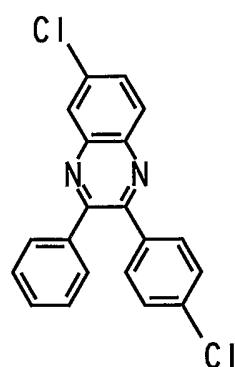
FIG. 9T



V(t)

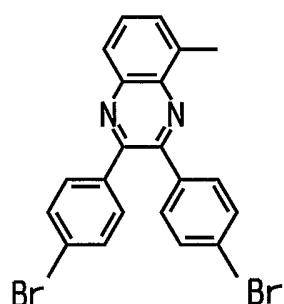
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FIG. 9U



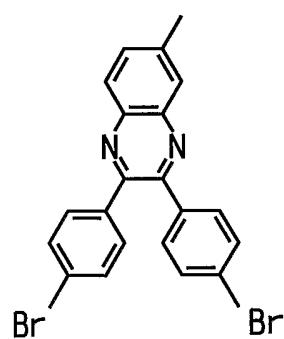
V(u)

FIG. 9V



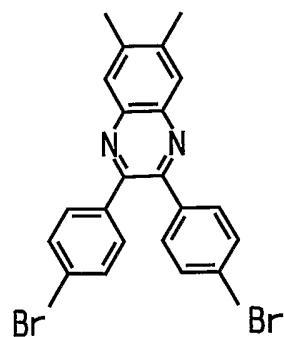
V(v)

FIG. 9W



V(w)

FIG. 9X



V(x)

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FIG. 9Y

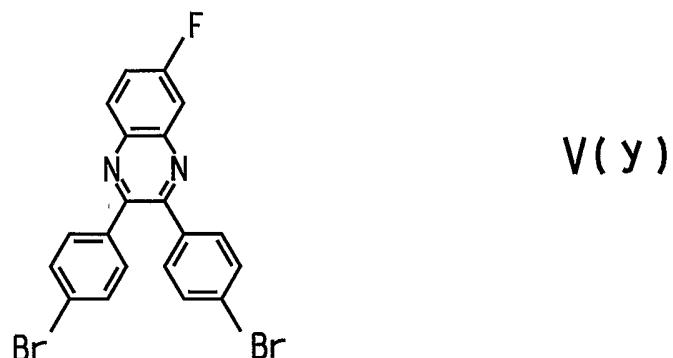


FIG. 9Z

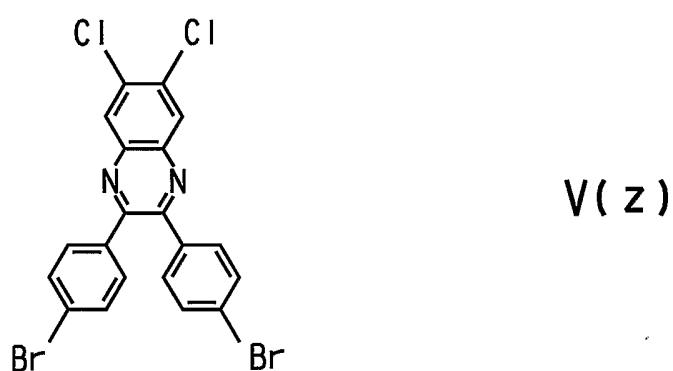


FIG. 9AA

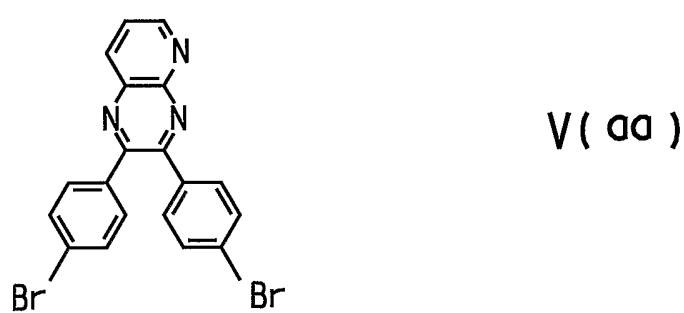
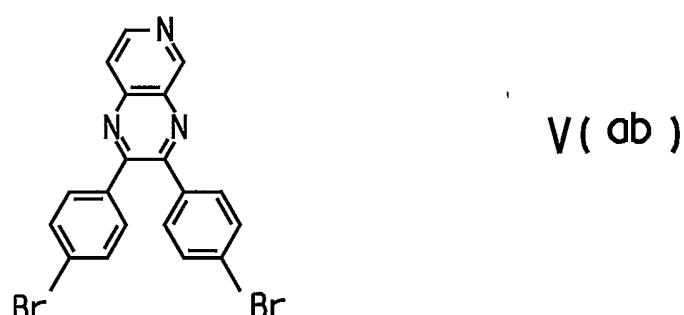
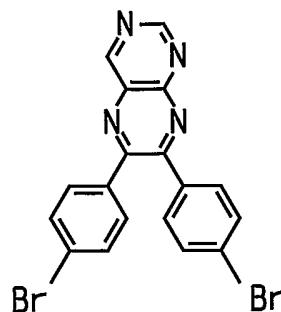


FIG. 9AB



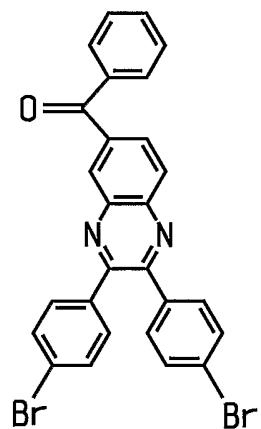
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FIG. 9AC



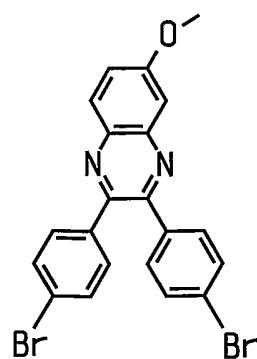
V(ac)

FIG. 9AD



V(ad)

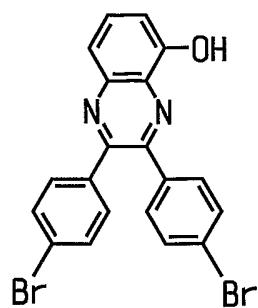
FIG. 9AE



V(ae)

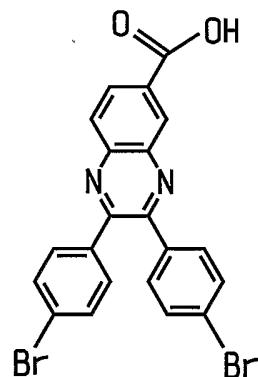
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FIG. 9AF



V(af)

FIG. 9AG



V(ag)

FIG. 10

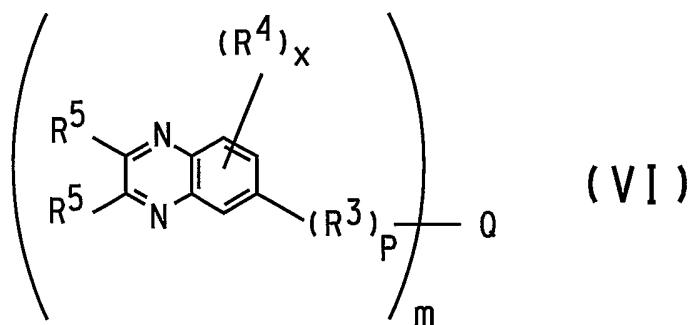
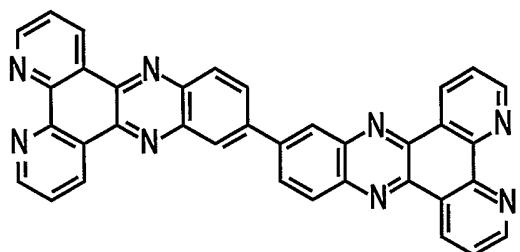
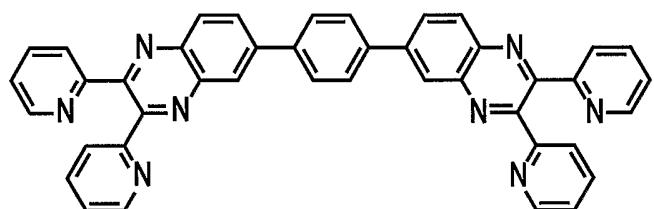


FIG. 11A



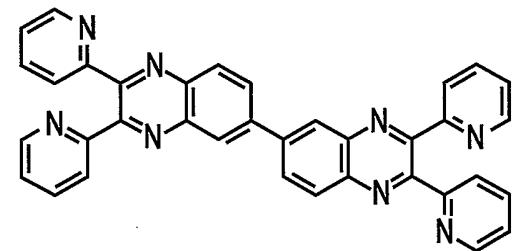
VI(a)

FIG. 11B



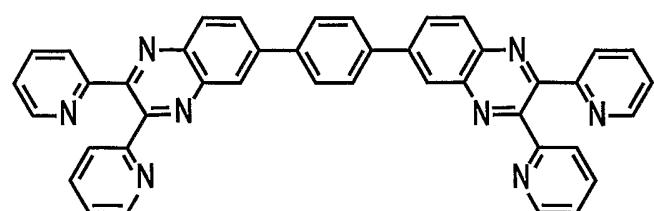
VI(b)

FIG. 11C



VI(c)

FIG. 11D



VI(d)

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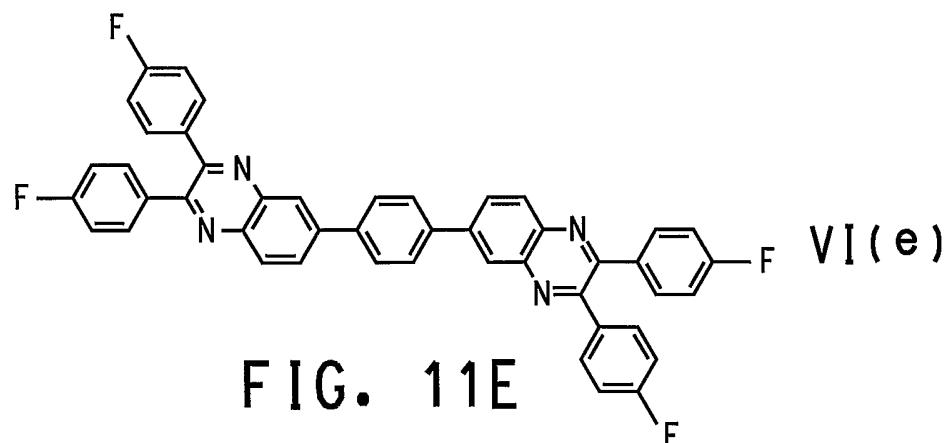


FIG. 11E

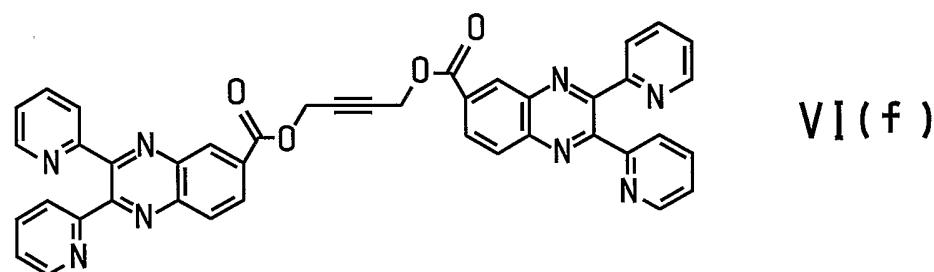


FIG. 11F

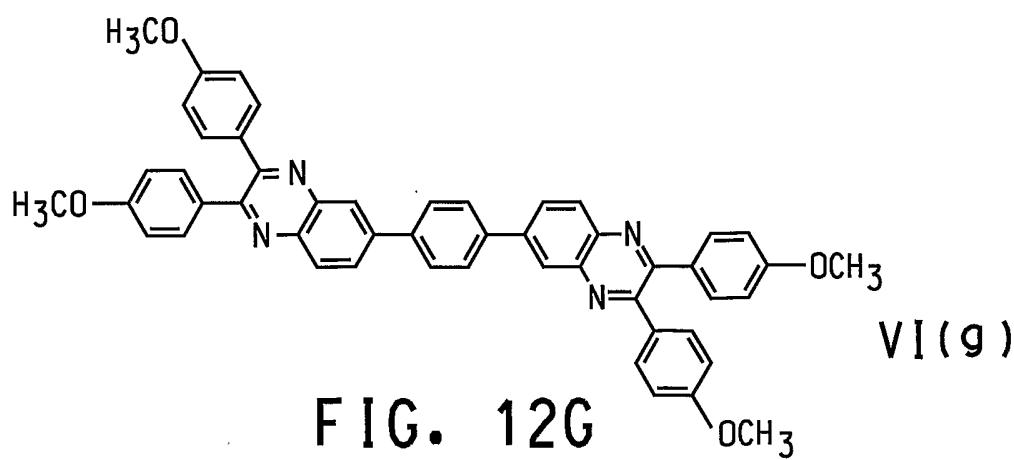


FIG. 12G

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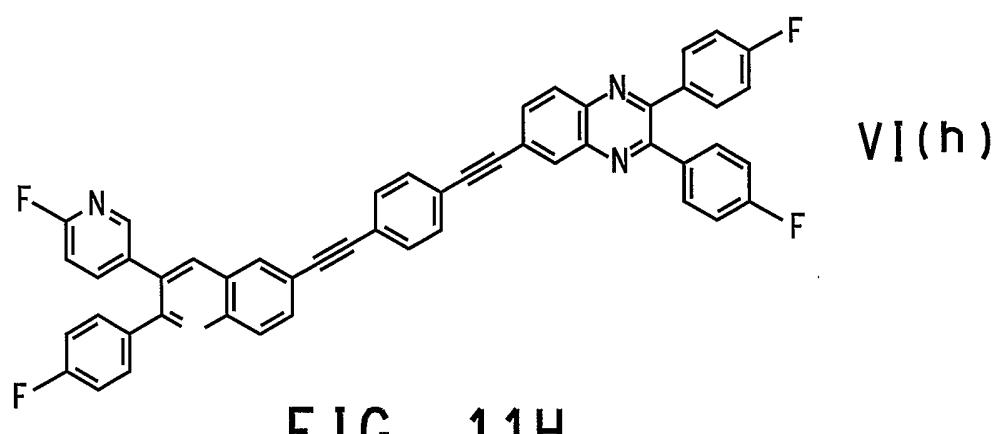


FIG. 11H

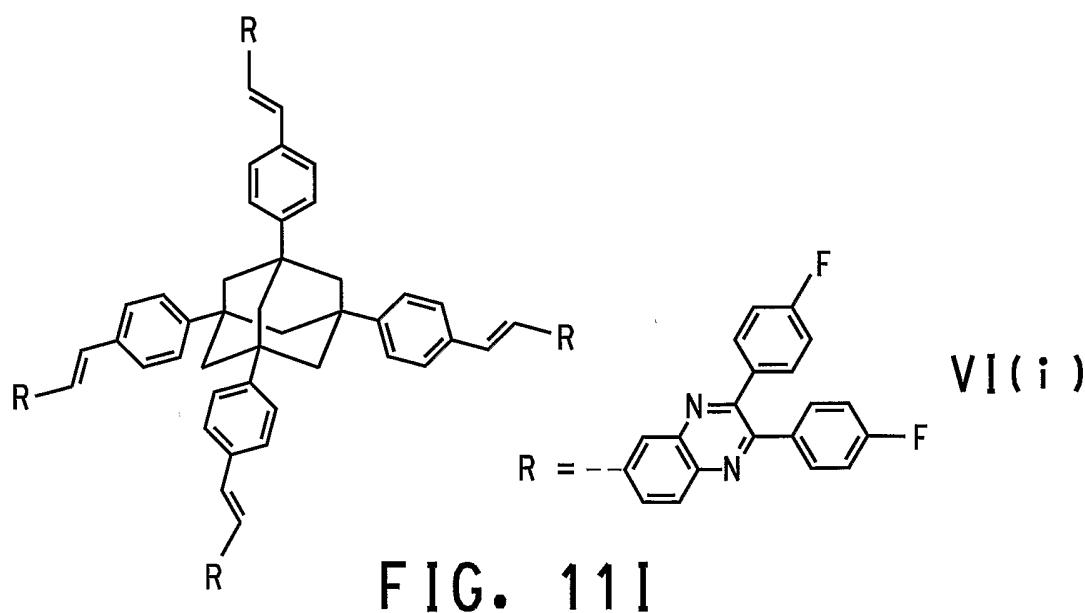


FIG. 11I

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FIG. 11J

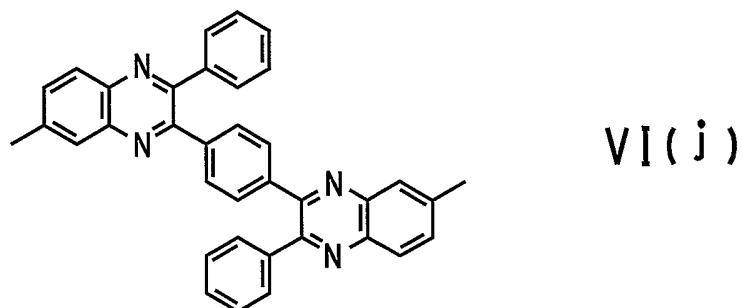


FIG. 11K

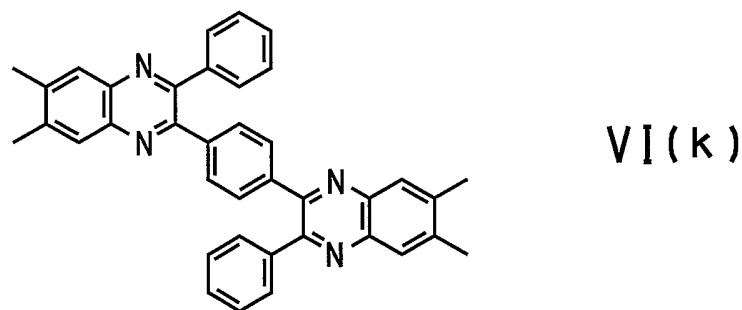


FIG. 12

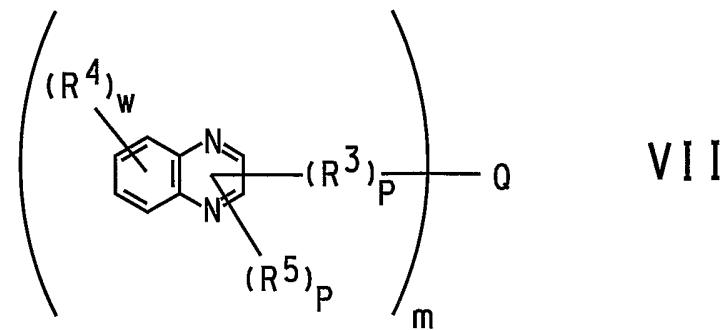


FIG. 13A

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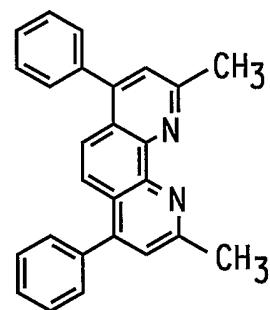
DDPA
(Compound A)

FIG. 13B

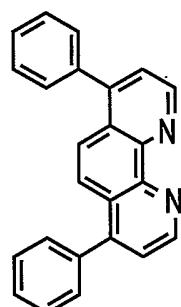
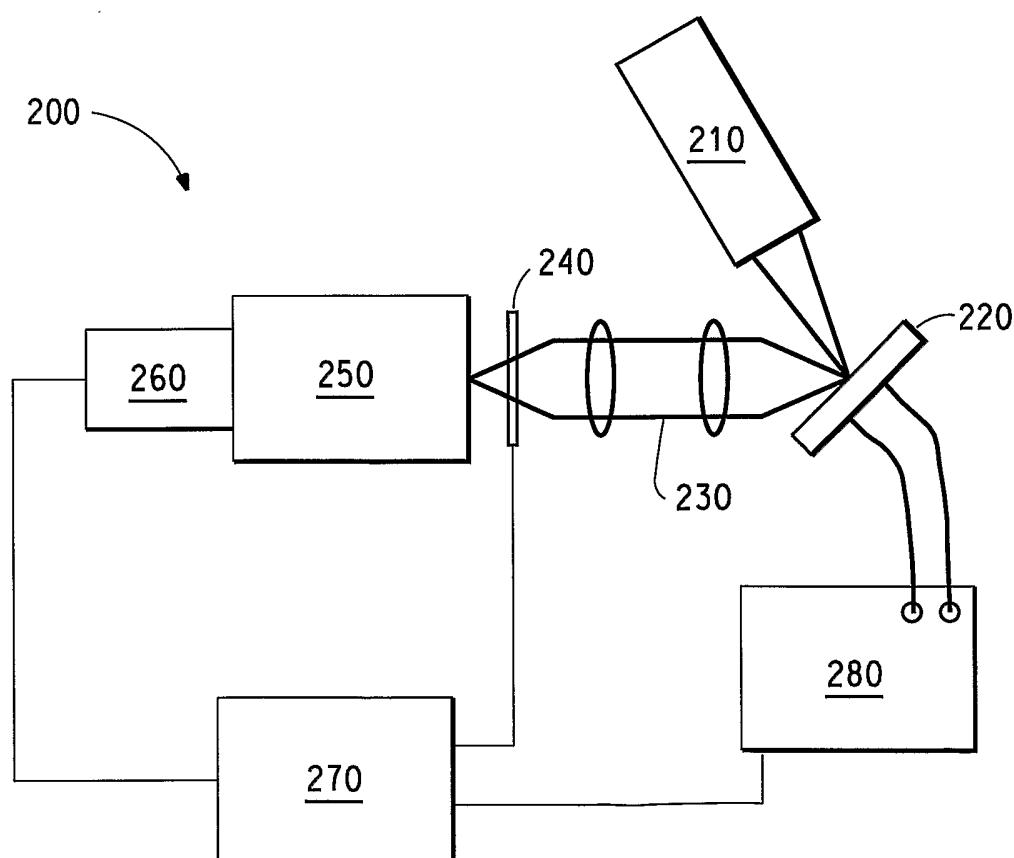
DPA
(Compound B)

FIG. 14

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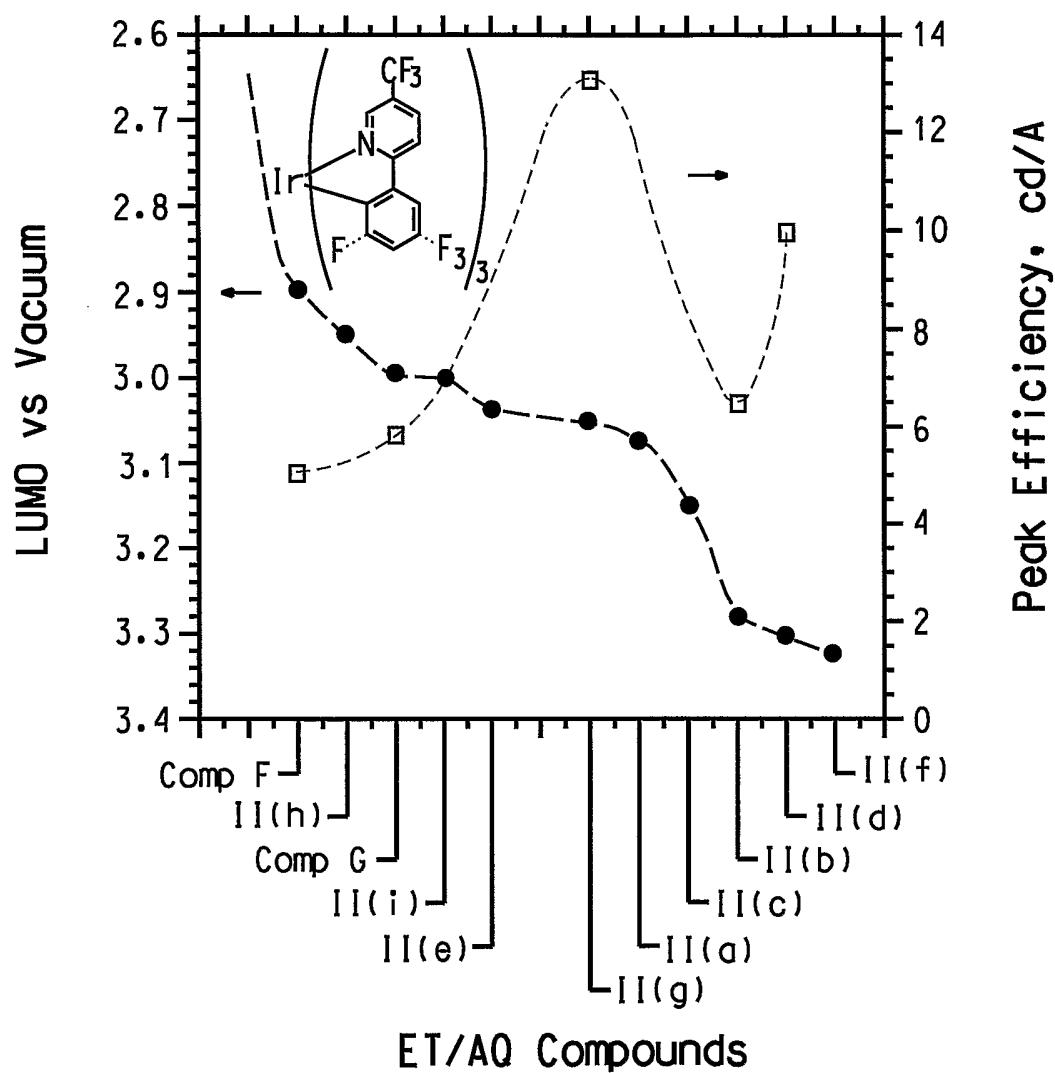


FIG. 15

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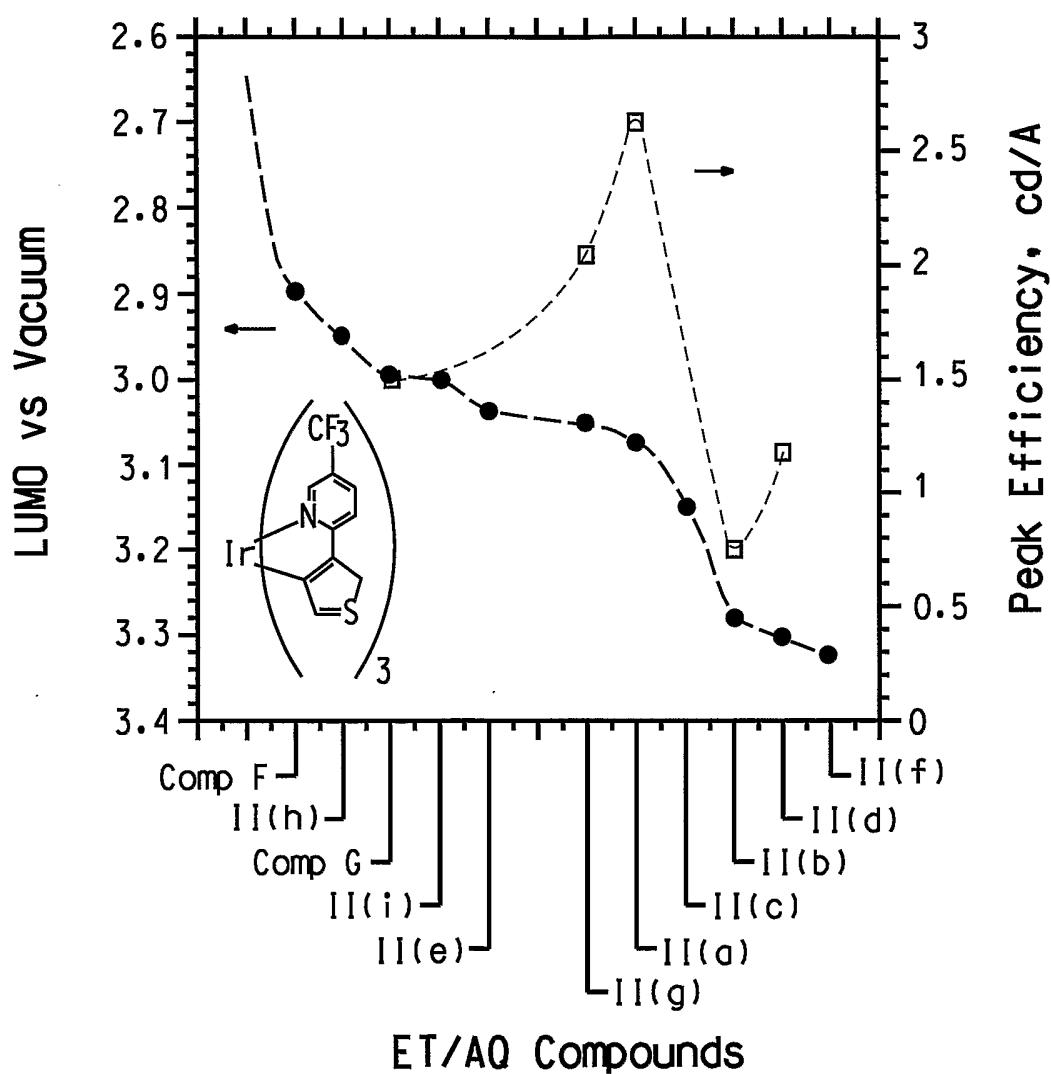


FIG. 16

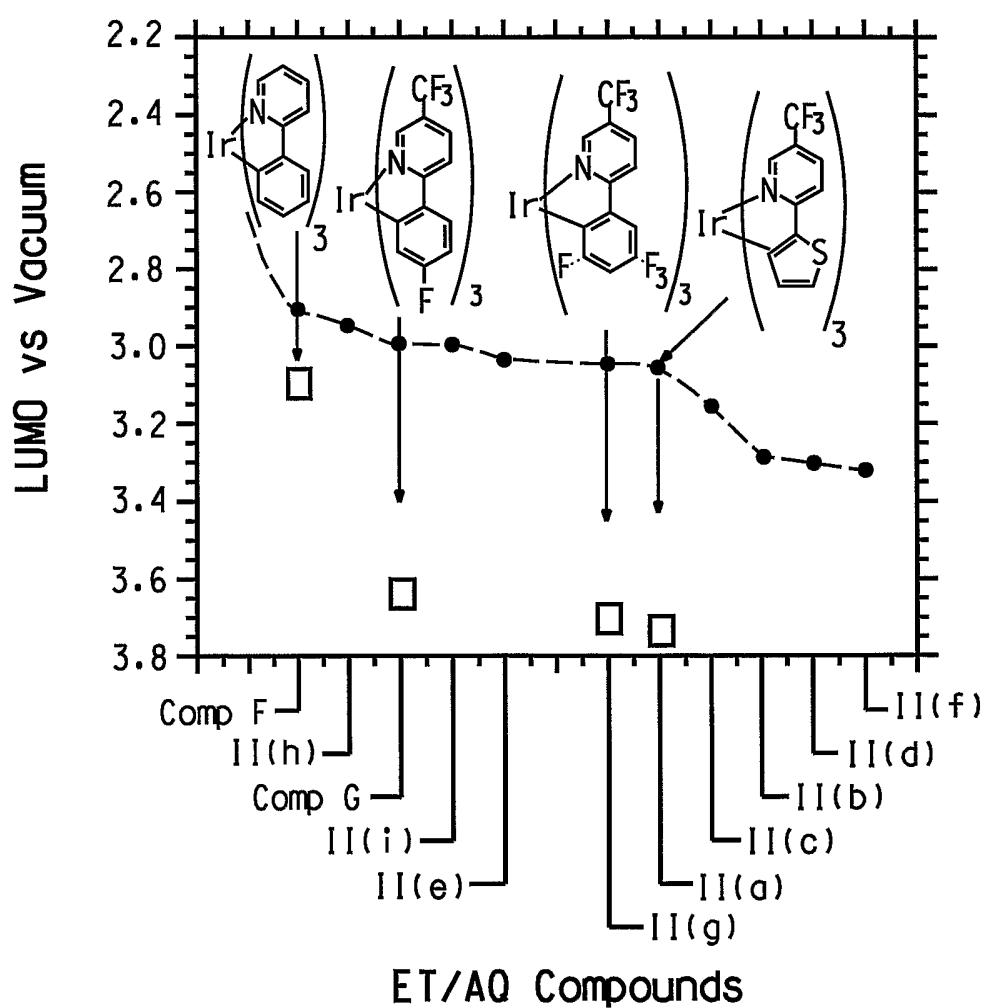


FIG. 17

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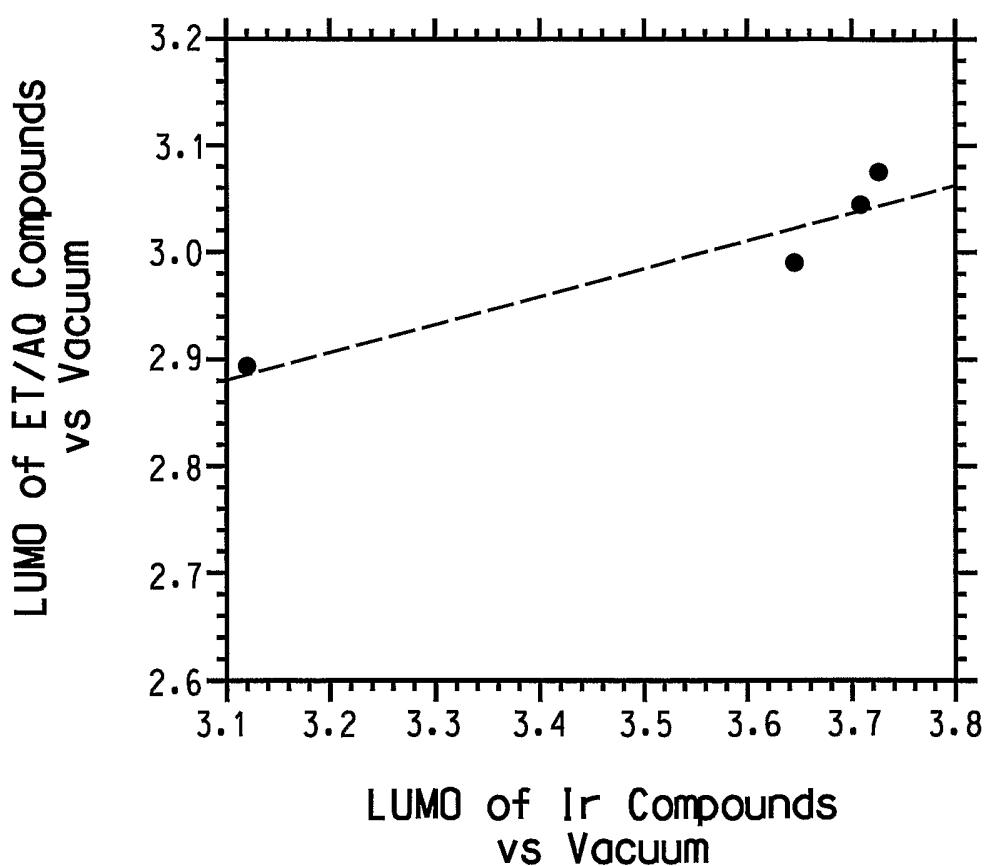


FIG. 18