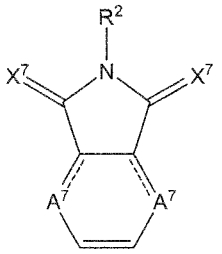


(VIIa)



(VIIb)

wherein

$\cdots\cdots$ is a single or double bond, as valency allows;

R^2 is an optionally substituted alkyl or optionally substituted aryl;

X^7 is O or S; and

A^7 is CH, CH_2 or N.

Advantageously, the compounds of formula (VIIa) or (VIIb) as defined above may be intrinsically electron-withdrawing, such that when reacted with the tetrazine compound having Formula (VI) as defined above, the resulting product will have ultra-high electron affinity. Further advantageously, the compounds of Formula (VIIa) or (VIIb) may be easy to functionalize. More advantageously, the compound of Formula (VIIa) or (VIIb) as defined above may be tunable by their R^2 functional group to enhance their solubility properties such that they may be useful in reactions performed in a variety of solvents.

In a fifth aspect, there is provided a method for synthesizing the compound of Formula (VI) as defined above, comprising the steps of providing a hydrazine and contacting the hydrazine with a functionalized cyclic group, wherein the cyclic group of the functionalized cyclic group is selected from the group comprising of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted tellurophene, optionally substituted pyrrole, optionally substituted phenylene, optionally substituted aza-phenylene, optionally substituted arylene diimide, optionally substituted fluorene, optionally substituted cabazole, optionally substituted dibenzodilole, optionally substituted benzooxodiazole, optionally substituted benzotriazole, optionally substituted benzothidiazole and any combination thereof.

In a sixth aspect, there is provided a method for synthesizing the compound of Formula (I) as defined above, comprising the steps of:

providing the compound of Formula (VI) as defined above; and

contacting the compound of Formula (VI) as defined above with the compound of Formulae (VIIa) or (VIIb) as defined above under reaction conditions to form the compound of Formula (I) as defined above.

Advantageously, the method for synthesizing the compound of Formula (I) as defined above may be an inverse-electron demanding Diels-Alder reaction. Conventionally, for Diels-Alder reactions that are being carried out on a tetrazine, the tetrazine acts as a diene and therefore should be modified with electron withdrawing groups to enhance its reactivity. Conversely, the dienophile should be modified with electron donating groups. This is to facilitate the inverse electron demanding Diels-Alder

reaction. However, in the synthesis of the compound of Formula (I) as defined above, the tetrazine moiety has two electron donating units P1 attached. In addition, the dienophile (compounds of Formulae (VIIa) or (VIIb) as defined above) is an intrinsically electron withdrawing imide. Under such conditions, the inverse-electron demanding Diels-Alder reaction has conventionally faced challenges due to the unfavourable electronic interaction between the tetrazine and the dienophile.

However, advantageously, the compound of Formula (I) may be synthesized with a good overall yield by the method as defined above. More advantageously, the successful synthesis may be due to judicious choice of reaction solvents, reaction temperature and reaction duration. Advantageously, the solvent used for the reaction may not contain any reactivity towards the reaction mixture. More advantageously, the boiling point of the solvent may be sufficiently high to allow the reaction to proceed. Advantageously, the method as defined above may enable the synthesis of the compound of Formula (I) with an isolated yield of higher than 90%.

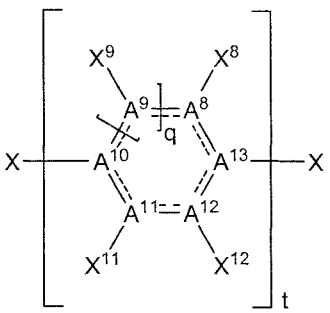
Further advantageously, the method as defined above is scalable. The compound of Formula (I) as defined above may therefore be synthesized at a larger scale of up to 500 g.

In an seventh aspect, there is provided a method for synthesizing the compound of Formula (IV) as defined above, comprising the step of:

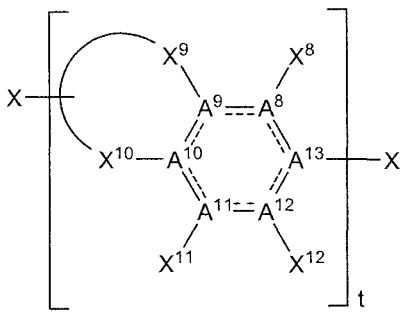
providing the compound of Formula (I) as defined above; and

contacting the compound of Formula (I) as defined above with;

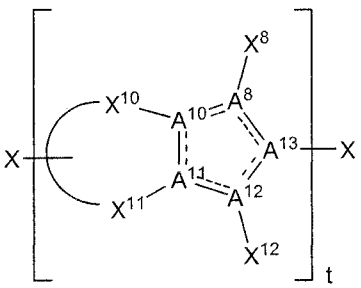
(i) a compound having the following Formula (XXVa), (XXVb) or (XXVc) ;



(XXVa)



(XXVb)



(XXVc)

wherein

$\overline{\overline{\quad\quad}}$ is a single or double bond, as valency allows;

q is 0 or 1;

t is an integer selected from 1 to 4;

X, X^8, X^9, X^{11} and X^{12} are independently absent or selected from the group consisting of a bond, H, halogen, CN, R^3, OR^3 or SR^3;

wherein R^3 is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A^8 is selected from the group consisting of O, S, Se, Te, C and N

A^9, A^{10}, A^{11}, A^{12} and A^{13} are independently C or N; and

wherein any two substituents selected from the group consisting of X^8, X^9, X^{10}, X^{11} and X^{12} may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl; and

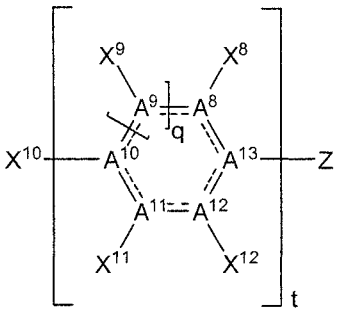
(ii) a cross-coupling reagent comprising a cyclic group; and an element selected from the group consisting of zinc, tin and boron; wherein the cyclic group is selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

in the presence of a metal-containing catalyst.

In an eighth aspect, there is provided a method for synthesizing the compound of Formula (IV) as defined above, comprising the steps of:

1) providing the compound of Formula (I) as defined above; and

2) contacting the compound of Formula (I) as defined above with a compound having the following Formula (XXVI);



(XXVI)

wherein

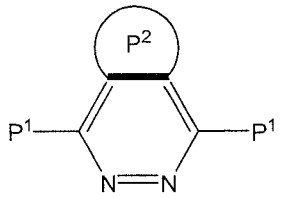
----- is a single or double bond, as valency allows;

q is 0 or 1;

t is an integer selected from 1 to 4;

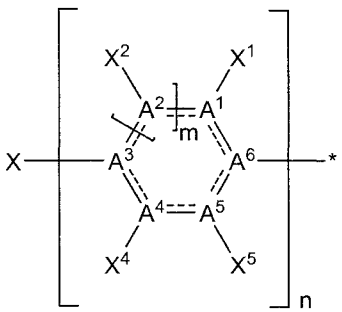
Claims

1. A compound having the following Formula (I);

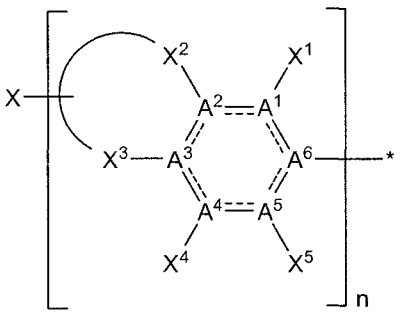


(I)

wherein P^1 has the following Formula (IIa) or (IIb);



(IIa)



(IIb)

wherein

$\overset{\text{- - - - -}}{\text{———}}$ is a single or double bond, as valency allows;

m is 0 or 1;

n is an integer selected from 1 to 4;

X, X^1, X^2, X^3, X^4 and X^5 are independently absent or selected from the group consisting of a bond, H, halogen, CN, R^1, OR^1 or SR^1;

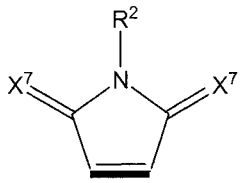
wherein R^1 is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A^1 is selected from the group consisting of O, S, Se, Te, C and N

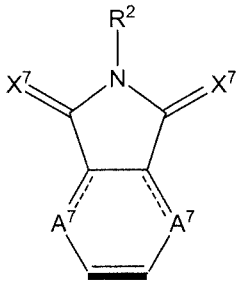
A^2, A^3, A^4, A^5 and A^6 are independently C or N; and

wherein any two substituents selected from the group consisting of X^1, X^2, X^3, X^4 and X^5 may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

and wherein P^2 has the following formula (IIIa) or (IIIb);



(IIIa)



(IIIb)

wherein

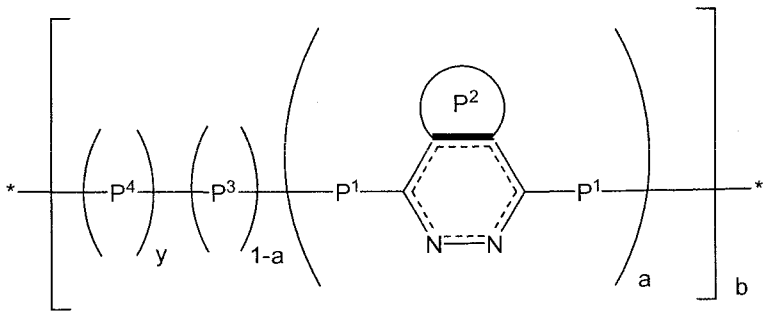
R^2 is an optionally substituted alkyl or optionally substituted aryl;

X^7 is O or S;

A^7 is CH, CH_2 or N;

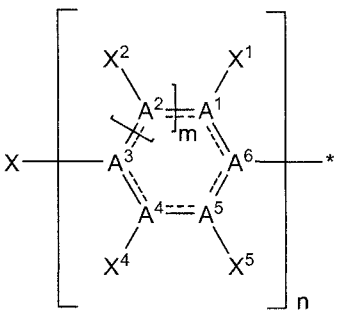
and —— is where the compound of Formula (IVa) or (IVb) is fused to the compound of Formula (I).

2. A compound having repeating units of the following Formula (IV);

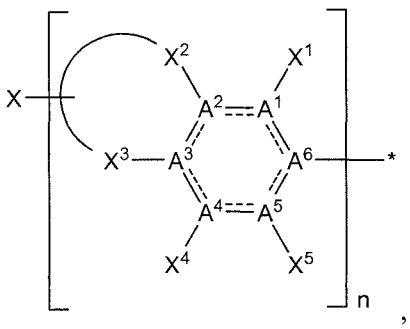


(IV)

wherein P^1 has the following Formula (IIa) or (IIb);



(IIa)



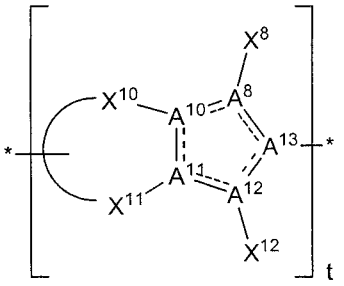
(IIb)

wherein

----- is a single or double bond, as valency allows;

m is 0 or 1;

n is an integer selected from 1 to 4;



(Vc)

wherein

q is 0 or 1;

t is an integer selected from 1 to 4;

X^8, X^9, X^{11} and X^{12} are independently absent or selected from the group consisting of a bond, H, halogen, CN, R^3, OR^3 or SR^3;

wherein R^3 is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A^8 is selected from the group consisting of O, S, Se, Te, C and N

A^9, A^{10}, A^{11}, A^{12} and A^{13} are independently C or N;

wherein any two substituents selected from the group consisting of X^8, X^9, X^{10}, X^{11} and X^{12} may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

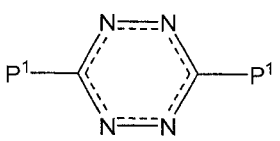
and P^4 is absent, or is an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.

a is any value from 0 to 1; and

b is an integer selected from 1 to 10,000; and

y is an integer selected from 0 to 5.

3. A compound having the following Formula (VI);



(VI)

wherein P^1 has the following Formula (IIa) or (IIb);