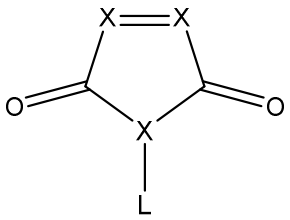
WHAT IS CLAIMED IS:

1. A method of coupling a functional group to a substrate, the method comprising:

providing an unsaturated cyclic dione coupled to a substrate; and

reacting the unsaturated cyclic dione with an indole or indazole including a first functional group to form a first adduct coupling the first functional group to the substrate and wherein the substrate comprises a solid support.

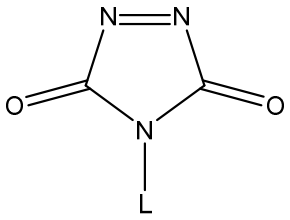
2. The method of claim 1, wherein the unsaturated cyclic dione is:



where L comprises a linker to the substrate and each X independently is CH or N.

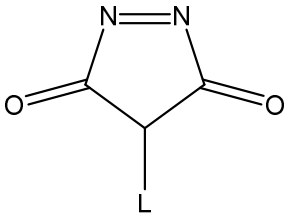
3. The method of claim 2, wherein the unsaturated cyclic dione is selected from any one of:

(i) triazolinedione:



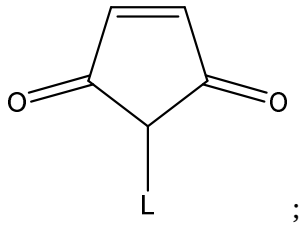
;

(ii) maleimide:



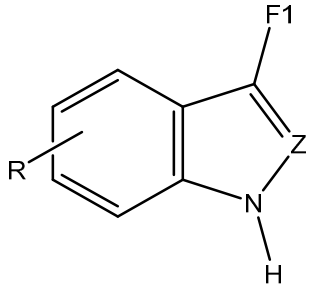
;

(iii) 4-cyclopentene-1,3-dione:



; optionally

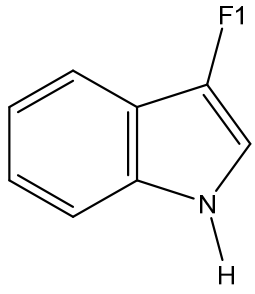
wherein the indole or indazole is:



where F1 comprises the first functional group; R is H, an electron withdrawing group, or an electron donating group; and Z is CH or N; further optionally

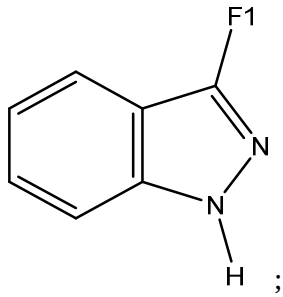
wherein the indole is selected from any one of:

(a) 1H-indole:



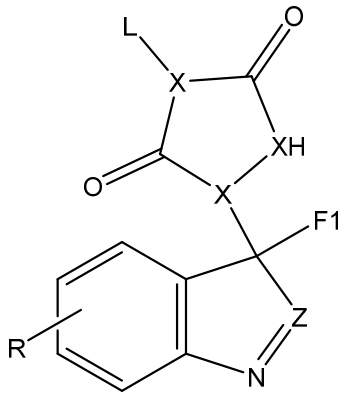
;

(b)1H-indazole:



;

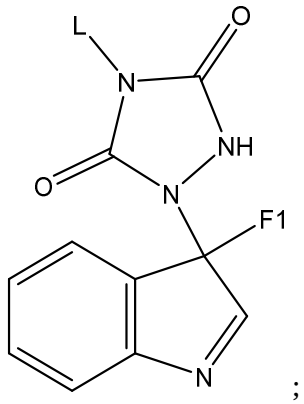
even further optionally wherein the first adduct is:



where L comprises a linker to the substrate and each X independently is CH or N.

4. The method of claim 3, wherein:

(i) the first adduct is:



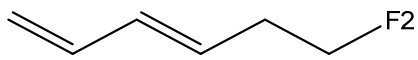
;

(ii) further comprising heating the first adduct to regenerate the cyclic unsaturated dione coupled to the substrate;

(iii) further comprising reacting the first adduct with a diene including a second functional group to form a second adduct coupling the second functional group to the substrate;

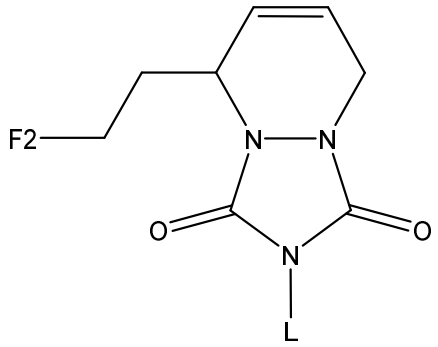
(iv) the diene comprises a 1,3-diene, optionally

wherein the 1,3-diene is:



where F2 comprises the second functional group, further optionally

wherein the second adduct is:



where L comprises a linker to the substrate; or

(v) any combination of (i) – (iv).

5. The method of claim 3 to 4, wherein:

(i) the first and/or second functional group is selected from the group consisting of: an oligonucleotide, a hydrophilic molecule, a catalyst, and a label, wherein the hydrophilic molecule is PEG; optionally

the second functional group is an oligonucleotide; or

(ii) the substrate comprises a polymer disposed on the solid support, optionally wherein the polymer is functionalized to include polyhedral oligomeric silsesquioxane (POSS); further optionally

wherein providing the unsaturated cyclic dione coupled to the substrate comprises:

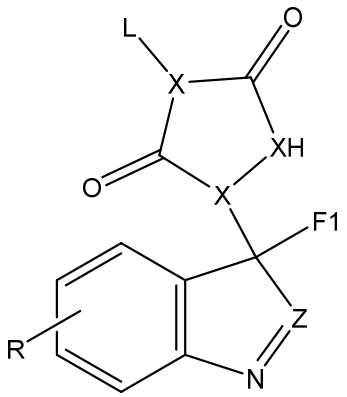
providing a 4-substituted urazole coupled to the substrate; and

oxidizing the 4-substituted urazole to form a triazolinedione.

6. A composition, comprising:

a substrate wherein the substrate comprises a solid support; and

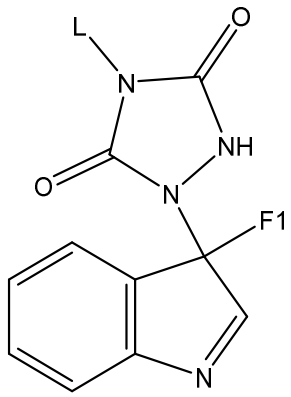
an adduct coupled to the substrate:



where L comprises a linker to the substrate; F1 comprises a first functional group; each X independently is CH or N; R is H, an electron withdrawing group, or an electron donating group; and Z is CH or N.

7. The composition of claim 6, wherein

(i) the adduct is:



; and/or

(ii) wherein the first functional group is selected from the group consisting of: an oligonucleotide, a hydrophilic macromolecule, a catalyst, and a label, wherein the hydrophilic molecule is PEG; optionally

wherein the first functional group is an oligonucleotide;

(iii) wherein the substrate comprises a polymer disposed on the solid support, optionally wherein the polymer is functionalized to include polyhedral oligomeric silsesquioxane (POSS); or

(iv) any combination of (i) – (iii).

8. A method of coupling a functional group to a substrate, the method comprising:

providing an unsaturated cyclic dione coupled to a substrate; and

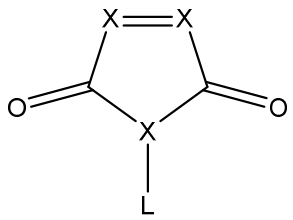
reacting the unsaturated cyclic dione with a diene including a functional group to form an adduct coupling the functional group to the substrate;

wherein the substrate comprises a polymer disposed on a solid support;

wherein the polymer the polymer is functionalized to include polyhedral oligomeric silsesquioxane (POSS).

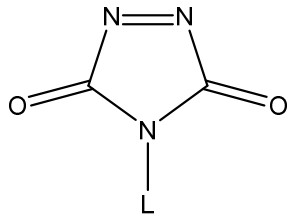
9. The method of claim 8, wherein:

(i) the unsaturated cyclic dione is:



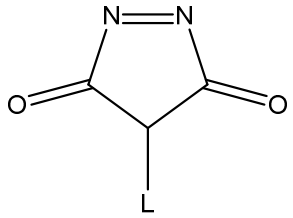
where L is a linker to the substrate and each X independently is CH or N, optionally wherein the unsaturated cylic dione is selected from any one of:

(a) triazolinedione:

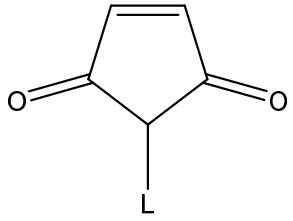


;

(b) maleimide:

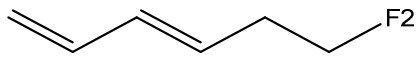


(c) 4-cyclopentene-1,3-dione:

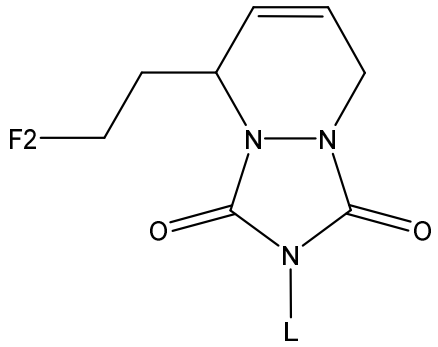


;

(ii) wherein the diene comprises a 1,3-diene, optionally wherein the 1,3-diene is:



where F2 comprises the functional group, further optionally wherein the adduct is:



where L comprises a linker to the substrate; or

(iii) a combination of (i) and (ii).

10. The method of any one of claims 8 to 9, wherein the functional group is selected from the group consisting of: an oligonucleotide, a hydrophilic molecule, a catalyst, and a label, wherein the hydrophilic molecule is PEG; optionally

wherein the functional group is an oligonucleotide.

11. The method of any one of claims 8 to 10, wherein providing the unsaturated cyclic dione coupled to the substrate comprises:

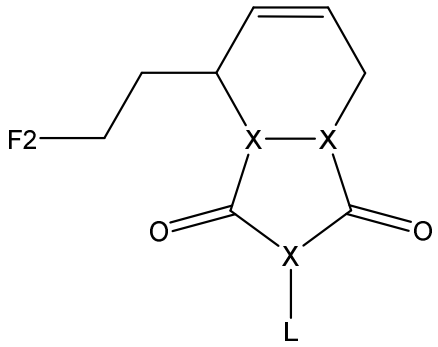
providing a 4-substituted urazole coupled to the substrate; and

oxidizing the 4-substituted urazole to form triazolinedione.

12. A composition, comprising:

a substrate;

an adduct coupled to the substrate:

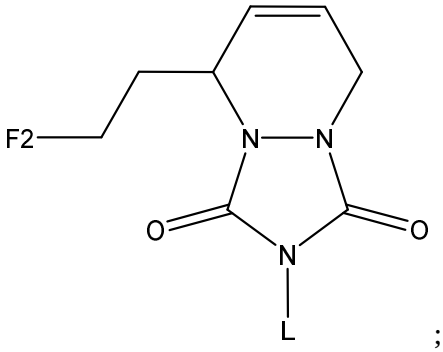


where L comprises a linker to the substrate, F2 comprises a functional group, and each X independently is CH or N;

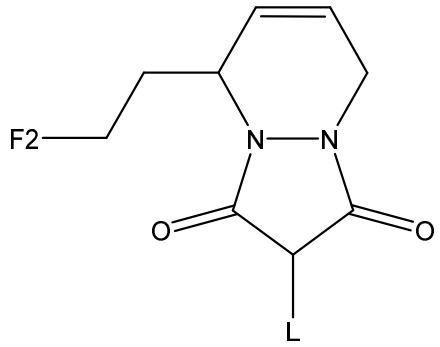
wherein the substrate comprises a polymer disposed on a solid support; and

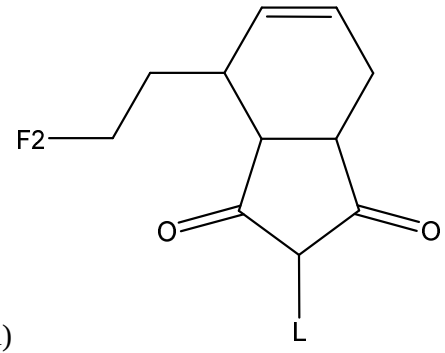
wherein the polymer is functionalized to include polyhedral oligomeric silsesquioxane (POSS).

13. The composition of claim 12, wherein the adduct is:

(i) 

;

(ii) 

(iii) 

; optionally

(iv) wherein the functional group is selected from the group consisting of: an oligonucleotide, a catalyst, and a label wherein the hydrophilic molecule is PEG; optionally wherein the functional group is an oligonucleotide; or

(v) any combination of (i) – (iv).

14. A method of coupling a functional group to a substrate, the method comprising:

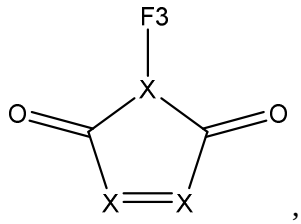
providing an indole or indazole coupled to a substrate; and

reacting the indole or indazole with a first unsaturated cyclic dione including an oligonucleotide to form a first adduct coupling the oligonucleotide to the substrate.

15. The method of claim 14, wherein:

(i) the first unsaturated cyclic dione is:

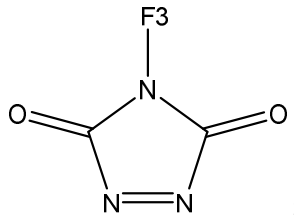
(a)



,

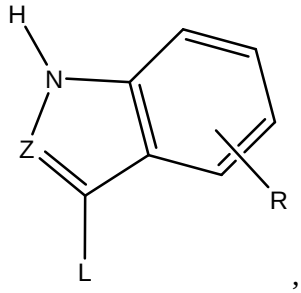
wherein F3 comprises the oligonucleotide and each X independently is CH or N or

(b) triazolinedione:



; optionally

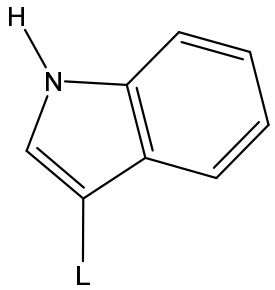
(ii) the indole or indazole is:



,

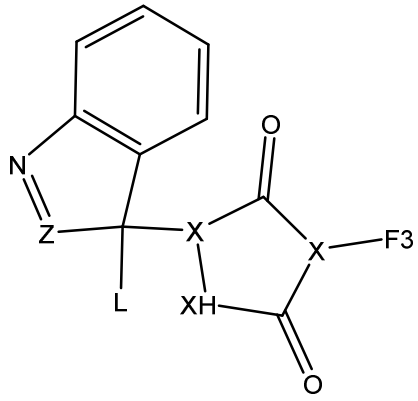
where Z is CH or N, L comprises a linker to the substrate, and R is H, an electron withdrawing group, or an electron donating group; or

the indole is 1H-indole:



where L is a linker to the substrate, optionally

wherein the first adduct is:



wherein F3 comprises the oligonucleotide, and each X independently is CH or N.

16. The method of any one of claims 14 to 15, further comprising:

(i) heating the first adduct to regenerate the indole or indazole coupled to the substrate; optionally

after regenerating the indole or indazole coupled to the substrate, reacting the indole or indazole with a second unsaturated cyclic dione to form a second adduct, further optionally

wherein the second unsaturated cyclic dione includes a functional group, even further optionally

wherein the functional group is selected from the group consisting of: a second oligonucleotide, a hydrophilic molecule, a catalyst, and a label, wherein the hydrophilic molecule is PEG:

(ii) wherein the substrate comprises a polymer disposed on a solid support, optionally wherein the polymer is functionalized to include polyhedral oligomeric silsesquioxane (POSS);

(iii) even further comprising:

providing a 4-substituted urazole including the oligonucleotide; and

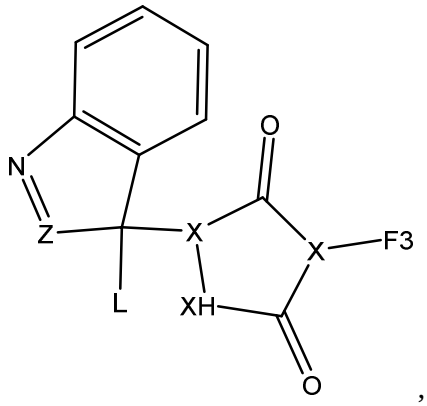
oxidizing the 4-substituted urazole to form the unsaturated cyclic dione triazolinedione including the oligonucleotide; or

(iv) any combination of one of (i)-(iii).

17. A composition, comprising:

a substrate; and

an adduct coupled to the substrate:

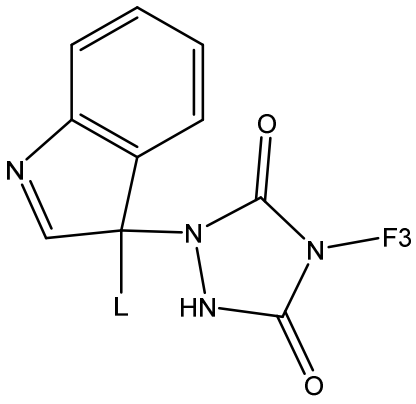


,

where L comprises a linker to the substrate, F3 comprises an oligonucleotide, each X independently is CH or N, and Z is CH or N.

18. The composition of claim 17, wherein:

(i) the adduct is:



, and/or

(ii) the substrate comprises a polymer disposed on a solid support, optionally wherein the polymer is functionalized to include polyhedral oligomeric silsesquioxane (POSS).

19. A method of coupling a functional group to a substrate, the method comprising:

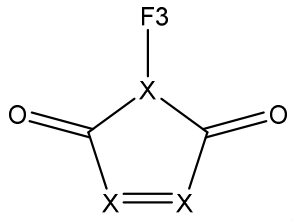
providing a diene coupled to a substrate; and

reacting the diene with an unsaturated cyclic dione including an oligonucleotide to form a first adduct coupling the oligonucleotide to the substrate.

20. The method of claim 19, wherein:

(i) the unsaturated cyclic dione is any one of:

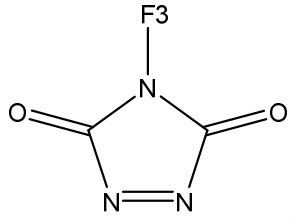
(a)



,

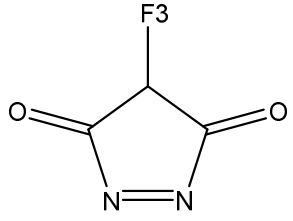
where F3 comprises the oligonucleotide and each X independently is CH or N;

(b) triazolinedione:



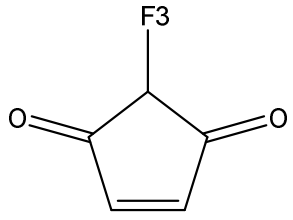
,

c) maleimide:



; or

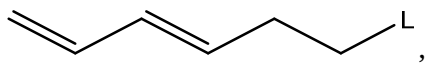
(d) 4-cyclopentene-1,3-dione:



; and/or

(ii) the diene comprises a 1,3-diene, optionally

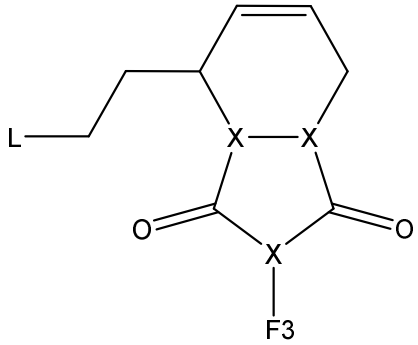
wherein the 1,3-diene is:



,

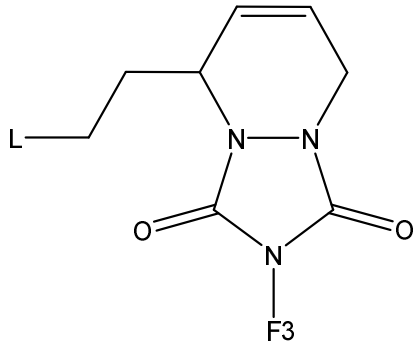
where L comprises a linker to the substrate;

(iii) the adduct is:



where L comprises a linker to the substrate, each X independently is CH or N, and F3 comprises the oligonucleotide, optionally

wherein the adduct is:



;

(iv) the substrate comprises a polymer disposed on a solid support, optionally wherein the polymer is functionalized to include polyhedral oligomeric silsesquioxane (POSS);

(v) further comprising:

providing a 4-substituted urazole including the oligonucleotide; and

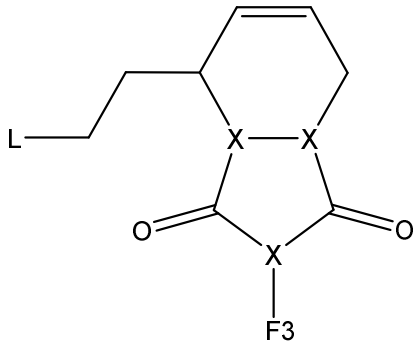
oxidizing the 4-substituted urazole to form the unsaturated cyclic dione triazolinedione including the oligonucleotide; or

(vi) any combination of (i) – (v).

21. A composition, comprising:

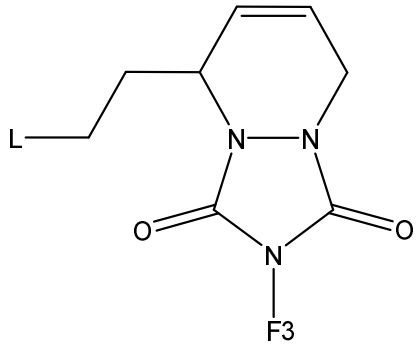
a substrate; and

an adduct coupled to the substrate:



where L comprises a linker to the substrate, each X independently is CH or N, and F3 is an oligonucleotide.

22. The composition of claim 21, wherein the adduct is:



; optionally

wherein the substrate comprises a polymer disposed on a solid support, further optionally wherein the polymer is functionalized to include polyhedral oligomeric silsesquioxane (POSS).