3000 words, not including references

Diazo and Diazonium Compounds for Surface Modification

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Abstract: This digest surveys recent trends in the development and application of diazo and diazonium compounds for the surface modification of diverse materials; the interest in these reagents derives both from their ready capacity to extrude nitrogen and in so doing generate reactive species, such as carbenes or radicals, or to react directly by diazonium coupling, with both processes easily capable of occurring at interfaces, leading to the modification of surface chemical functionality without alteration of the bulk material.

The development of rapid chemical conjugation methodologies suitable for small molecule synthesis (such as catalyzed ligand coupling[1, 2] and Click reactions[3]) over the last two decades has changed the way applications of chemical synthesis in drug discovery,[4, 5] biomedical science,[6] and device[7] and polymer[8] construction are conceived and perhaps more importantly has opened opportunities for their routine use by chemical non-specialists. A similar development in capability is now occurring for chemical reactions which permit the direct and rapid functionalization of the surfaces of diverse materials;[9] such capacity is important in device fabrication and biomedical applications where it can be highly advantageous to be able to control surface properties independently of the bulk material properties. Nitrogen-containing chemical species – diazo and diazonium functionalities – are emerging as ideal candidates either for direct coupling, or after extrusion of nitrogen under thermal or photochemical conditions, to generate highly reactive species (carbenes, nitrenes, radicals, carbocations) capable of reacting at a surface with covalent bond formation. This digest outlines recent developments – and cautions – in this area. A detailed review of the functionalization of polystyrene and their applications has appeared.[10]

Diazonium reagents

Diazonium reagents, readily prepared by diazotization of amines under a variety of conditions, may be used for surface modification, by direct reaction leading to the formation of an azo linkage (which, incidentally, also generates a visible azo-chromophore) or by single electron transfer with extrusion of nitrogen leading to a radical intermediate, which then reacts with the surface, in a process analogous to the Gomberg-Bachmann reaction; these processes are discussed in more detail below.

Here, two methods are listed, and azo bond linkage is used as a subtitle, so I think the "radical intermediate" should also be added as a subtitle(see below).

Azo bond linkage

The simplest and most well-known reaction of diazonium salts is with electron-rich compounds to form an azo-link, and the mildness of the conditions allows this approach to be widely used for biological materials. Thus, a diazonium unit immobilized on agarose has been shown to be capable of reaction with exposed tyrosine residues, and for the modification of protein.[11] Graphene oxide, modified with a spacer which terminates in a diazonium group, has been used for the rapid immobilization of cellulase; this was found to proceed efficiently, to significantly stabilize the enzyme, and to enhance catalytic activity (Scheme 1).[12] Diazonium species have even been used for the anchorage of polymers onto the surface of viruses, which are designed to mask surface proteins and modulate the viral pharmacokinetic profile; the efficiency of this process was found to depend upon polymer chain length and the density of reacting diazonium groups.[13]

change to "for example"

subtitle"Radical intermediate" here?

The generation of radicals by redox collapse of diazonium salts, mediated by electrochemistry, photochemistry, reductants or reducing surfaces, has been widely used for surface modification. The kinetics of the electrodeposition of diazonium salts onto a gold surface has been examined by Electrochemical Quartz Crystal Microbalance and shown to follow a two-step deposition process which begins with the formation of a monolayer **1** (Step A, Scheme 2) followed by the very rapid growth of multilayers **2** (Step B, Scheme 2), especially for $R=NO_2$.[14] It was found that electron-withdrawing substituents R on the diazonium salt favour the reaction of aryl radicals on gold, and that radicals react approximately one order of magnitude faster on gold than on carbon substrates. Of interest, though, is a detailed study of the surface modification of conducting metal or carbon substrates both by electrochemical reduction of diazonium salts and by dipping of the diazonium substrate solution which suggests that surface modification is more complex;[15] considering the simple phenyldiazonium case, although there is general agreement that polyphenylene layers of type **3** are formed, clear TOF-SIMS experimental evidence has been found which shows that azo bonds are also formed in the covalently bonded surface layers. These outcomes could arise by reaction of the first formed monolayer **1** (R = H) either with phenyl radicals to give homopolyphenylene **3** or with the reactive diazonium salt to give an intermediate radical cation ultimately leading to multilayer **4**, or conceivably by direct azo-coupling of the diazonium salt to give rise to the product **5**; this process would be more favourable for electron rich substituted aromatic residues, such as **1** (R = electron releasing group), leading to multilayers of type **2**. The mechanism of layer growth by the reduction of diazonium salts with 2,2-diphenylpicrylhydrazyl has been found to occur by redox cross reactions. Control of the surface coverage is possible by adjusting the concentration of the redox mediator and this is reported to enable near-monolayer formation.[16]

Diazonium salts have been found to be highly effective for reaction with the abundant sp^2 carbons in graphene sheets;[17] however, a caution has been noted: the use of sodium nitrite under aqueous conditions for diazotisation runs the risk of the generation of phenolic by-products which may physisorb on the surface, rather than covalently attach as would be expected of radical coupling (Scheme 3).[18]

Radical modification has been widely used in carbon allotropes, including fullerenes[19] and carbon nanotubes[20, 21] for the introduction of a diversity of properties.[22] Thus, substituted phenyl groups have been grafted onto the surface of graphene quantum dots to introduce photoluminescence that was blue-shifted; while the shift was independent of substituent, although did depend on the number of surface-grafted aryl groups.[23] The photochemical surface reaction of phenazine diazonium salt with graphene leads to a monolayer where molecules project from the surface with the maximum coverage of 0.25 molecules per graphene unit cell.[24] The adsorption and grafting of phenyl and *p*-nitrophenyl diazonium cations onto graphene oxide has been studied by density functional theory (DFT); the most probable adsorption sites were found but most importantly the instability of aryldiazonium cations means that the grafting reaction is energetically barrierless and leads to a thermodynamically stable surface.[25] The surface of electrodeposited graphene-coated carbon steel has been covalently modified with diazonium salts, substituted with *o*, *m*, and *p*-COOH, NO_2 and CH_3 groups, and their effect upon corrosion resistance investigated; the resulting aryl insertions were found to restore graphene defects and the *p*-methyl group in particular was found to give enhanced corrosion protection.[26] Organic films have been grafted onto a glassy carbon surface using 4-nitrobenzenediazonium salt by constant potential electrolysis for durations varying from 1 to 300 s; the terminal NO_2 groups were converted into NHOH and NH_2 groups by further electrolysis and the electrochemical behaviour of the resulting organic films characterised.[27]

A calix[4]arene-monodiazonium cation **6** in which the diazonium group is located on the large rim may be reduced electrochemically at glassy carbon electrodes to form compact covalently bound layers (Figure 1).[28] Electrochemically mediated aryl diazonium salt modifications on anode graphite fibre brushes have been studied; this has been shown to improve electron transfer from the electrode surface in microbial fuel cells.[29] The reaction of pentafluorophenyldiazonium salts with a carbon surface structured with ordered monodisperse pores has shown that the accessible surface was readily modified, rendering it hydrophobic, but that the inner micropores, which were not accessible to the larger aryl radicals, were in fact modified by nitroso radicals generated in the diazonium forming step, rendering them hydrophilic.[30] The synthesis of a bis(diazonium) salt **7** has been reported, along with its immobilization on high-surface-area Ketjen black carbon (Figure 1).[31] This material was redox-active and could be cycled at high rate with the maintenance of a faradaic contribution even after 6000 charge/discharge cycles. The modification of carbon fibre by electrochemical grafting with substituted diazonium salts **8** (R = H, *m*-CF_3, *p*-CO_2H, *p*-CO_2Na, *p*-$CONH(CH_2)_5CH_3$) has demonstrated that resistance could be increased between 25 - 81%, without loss of tensile strength or Young's modulus. Significantly better increases in resistance could be obtained by electrographing at high reductive potential (−1 V) for extended periods using diazobenzene, under which conditions thicker phenylene layers became deposited.[32] Exfoliation of graphite can be achieved by mechanical shear using ball milling with simultaneous surface reaction with variously substituted aryl diazonium salts **8** (R = *p*-Br, *p*-CO_2Et, *p*-Bu, *p*-$OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$).[33] The electrochemical reduction of pyridinediazonium salts **9a-c**, derived from 2-, 3- and 4-aminopyridine, has been used to modify the surface of carbon electrodes (Scheme 4). Interestingly, the behaviour of each at the surface is different, so that the pyridine-3-diazonium systems gives thicker layers than the 2- and 4-isomers. Using the latter, it is possible to prepare homogeneous, hydrophilic, dense, compact films which are sufficiently thin that fast electronic transfer rates can be achieved. When these are used in microbial fuels cells as graphite anodes, they show improved performance over bare graphite anodes.[34] Surface modification of glassy carbon via electrochemical reduction of an *in situ* generated urazole-substituted diazonium salt, followed by an Alder-ene reaction with a citronellyl derivative, yields material which exhibits enhanced electrochemical or wetting behaviour, depending on whether the citronellyl substitution contains a ferrocenyl **10a** or perfluoro-oligomeric **10b** substituent, respectively (Scheme 5).[35]

Fluorine-doped tin oxide (FTO) electrodes were surface modified by electroreduction of *in situ* generated 4-carboxyphenyl diazonium salt but this gave poorly-packed organic multilayers on the electrode surface (Scheme 6).[36] Electrochemically mediated modification of PEDOT onto platinum with diazonium salts gives films which do not suffer delamination even over redox 1000 cycles nor after ultrasonic treatment; this is important for neural sensing applications (Scheme 7).[37]

Modification of the surface of titanium alloy Ti6Al4V by 4-hydroxymethylbenzenediazonium salt gives a complete coating with variable thickness but which is stable in simulated body fluid.[38] The surface modification of CoCr alloy by electrodeposition with the diazonium salt derived from *p*-phenylenediamine and sodium nitrite gives layers which are stable under aqueous conditions and at various pH levels due to the hydrolytic inertness of the newly formed C–M bond. Of interest, though, is that a passivating oxide layer on the metal surface hinders electrografting of the diazonium salt.[39] Importantly, this surface treatment gives enhancements in the adhesion of PMMA to CoCr with tensile bond strength values similar to that of silane and phosphonate-based adhesives; it is suggested that this arises from improved entanglement and hydrogen bonding between the amine groups of PAP and the carbonyl groups of PMMA at the interface. This strategy has been used for the development of metal composite adhesives in which each amine group is activated sequentially, first to give modification at mirror-polished metallic surfaces, and secondly, to give polymer grafting with bisphenol A-glycidyl methacrylate; this has been developed for composite adhesives for dental alloys.[40] The chemical inertness and poor wetting properties of boron nitride nanotubes has been modified using the bis-diazonium salt derived from *p*-phenylenediamine by diazotisation with sodium nitrite, and the newly introduced amine groups offer the possibility of further surface modification (Scheme 8).[41]

In an approach which is complementary to this diazo-mediated protocol, iodonium salts have recently been used for the patterned surface modification of gold using photomasking; photosensitized irradiation with blue light generates nitrophenyl radicals, which insert into the surface to produce a polyaryl film (Scheme 9).[42]

Diazirines

Diazirine (CH_2N_2), a photoreactive gas used to generate methylene carbene (:CH_2), has been used for the study of protein conformation, structure and folding, since it is approximately isosteric with water,[43-45] and amino acid-derived diazirines have been used for a similar purpose.[46, 47] The relative stability of diazirines along with their convenient if multi-step chemical synthesis coupled with ease of chromatographic purification, has enabled their use for the modification of nylon[48] and glycoengineering[49] and this success has been more recently followed by successful application to the surface modification of graphitic and carbon nanotubes;[50] however, the formation of the diazirine was complicated by the presence of a photochemically-inactive azine impurity which

convenience?

could not be removed despite careful attempts at separation, and which to some extent obviated the advantages of using the diazirine system. In a different approach, thiol tether which terminates in a trifluoromethyldiazirine residue **11** has been attached to gold nanoparticles giving material **12** (Figure 2); photolysis during extended periods of irradiation (≥ 13h) gave insertion into acetic acid, methanol, benzyl alcohol, phenol, benzylamine, methyl acrylate, styrene and mannose.[51, 52] It was shown that irradiation of the diazirine could lead to direct formation of the carbene but evidence for isomerization to the diazo intermediate before collapse to the carbene was also obtained. Monolayers on thin, nanoporous silicon nitride membranes have been formed using the carbene derived from diazirine **13**, generated by vapour phase deposition with UV irradiation for 90min, and subsequent modification with PEG_{1000}-NH_2.[53] This modification has been shown to have such a low coating thickness (~7 nm) that gas and hydraulic permeability is retained; the surface modification is hydrolytically stable for up to 48 h of exposure to water and can suppress nonspecific adsorption of the proteins such as BSA and IgG. Extended photolysis for 12h of diazirine **14** has been used to modify the surface of graphene and microdiamond.[54] A diazirine-conjugated fluorescein **15** upon photoirradiation with silica nanoparticles gives surface modified material with good fluorescent stability and low cytotoxicity, and which may be used for *in vitro* cellular imaging.[55]

Diazo reagents

With the loss of gaseous nitrogen only but no other side products, diazo compounds may be used for surface modification under thermal or photochemical conditions, to give highly reactive carbenes which are capable of insertion and addition reactions. Although the parent system diazomethane is both readily accessible but dangerously unstable, substituted systems are much more tractable and are readily accessible either by conversion of a ketone to its hydrazine and oxidation or by Bamford-Stevens chemistry; astonishingly, natural products containing the diazo function are known where the same reactivity is exploited for modification of biomolecules.[56] Also of considerable interest is the recent emergence the possibility of C-1 carbene polymerization leading to direct polymer modification rather than surface modification only.[57]

hydrazone?

Our original report on the use of diaryldiazomethanes **16** for the modification of materials was, in retrospect, simplistic and limited in scope but did at least demonstrate the feasibility of the concept.[58] To achieve a useful modification, we found that it was necessary to use a two-step strategy in which surface modification of an otherwise inert material by carbene insertion in a first stage to generate **17** was followed by coupling with a suitably modified diazonium salt giving material **18** (Scheme 10); thus, the second stage made use of the diazonium-coupling strategy outlined above.[59, 60] Diaryldiazomethanes substituted with electron donating groups (**16**, X = MeO,

Me_2N) were much more reactive than for electron withdrawing groups (X = NO_2) for both Stages 1 and 2, but they were also more difficult to handle and needed to be used quickly (within 24 - 48h of synthesis). A key to the success of this strategy came with the realization that the effective surface modification during Stage 1 could only be achieved by initial physisorption of the diaryldiazomethane **16** onto the desired material surface by careful solvent removal, avoiding diazo collapse, followed by separate thermal or photochemical activation; attempted insertion using a heterogenous mixture of a solution of the diazo **16** and the material substrate failed completely. The surface loading density after carbene modification was in the region of 10^{13} molecules.cm^{-1}, that is approaching the same loading expected of a self-assembled monolayer, and suggesting that the physisorption step indeed led to SAM formation at the surface.[61, 62] This two-step sequence was operationally simple, and allowed sufficient flexibility that a carbene of appropriate reactivity capable of reaction with any surface could be identified in the first stage, and then the desired surface property could be introduced separately in the second one. Detailed work was subsequently undertaken to understand the first, carbene insertion, step in more detail and to clearly demonstrate that covalent surface modification had been achieved, even if direct observation of the new bond(s) formation was not possible.[62, 63] However, single step modifications were also feasible on occasions when more highly substituted diaryl diazo compounds were synthetically accessible, provided that the additional substitution could survive the carbene generating step by thermolysis or photolysis. Importantly, we were able to demonstrate the introduction of a variety of surface physical properties, including fluorescence,[64] wetting,[61, 65] and photochromicity.[66] Moreover, the level of surface modification was sufficient that metal binding,[67] protein binding[68, 69] and cell growth could be mediated,[70] and that the binding and release of peroxide could lead to observable antibacterial activity.[71, 72] This approach was found to be applicable to a wide range of substrates, including organic and inorganic materials and polymers which might otherwise be considered to be chemically inert[61] along with several allotropes of carbon – graphene, carbon black, nanotubes and diamond.[64, 73-75] Thus, the effective bulk crosslinking of graphene with HEMA(2-hydroxyethyl methacrylate or adhesion of carbon black with polypropylene leading to modified electrical conductivity could be achieved.[73, 75] We have more recently shown that this approach may be extended to more inert substrates such as polyethylene by activation with surface plasma treatment.[76, 77] A recent development has been the extension to bisdiazo systems **19** which give an excellent balance of synthetic accessibility, reactivity and scope[78-81] for the introduction of diverse surface function, and in particular antibacterial activity to several substrates.[82] Of particular interest is that the diaminobisdiazo system **19** (X = H_2N) is synthetically readily available and surprisingly stable, notwithstanding the presence of the free amine groups, unlike diamino system **16** (X =

the first step,carbene insertion,in more detail

Me_2N), and can be used for the surface manipulation of a variety of materials, in which the terminal amine functions also provide convenient chemical handles for further manipulation.

Copolymers which incorporate pendant diazomalonates can be activated by heat or light to generate the corresponding carbene, which undergo C-H insertion crosslinking with a variety of polymers, including PMMA, cyclic olefin copolymer (COC), poly(carbonate) (PC), PS, polyethylene (PE), poly(etheretherketone) (PEEK), or a polydimethylsiloxane (PDMS) by either dip or spin-coating, and have been shown to modify wetting behaviour and interactions with biomolecules (Scheme 11).[83]

Such applications have stimulated interest in understanding the surface chemistry at a fundamental level; a theoretical investigation using DFT analysis of the addition of triplet carbene (CH_2), silylene (SiH_2), germylene (GeH_2), and nitrene (NH) onto a diamond (100) surface has been reported. This shows that the reaction profiles for the additions of triplet species are different from those for singlets.[84] α-Acyldiazo functions have been used for on-surface reactions which have been studied at the fundamental level.[85] The surface reactions of bis(diazoketone) **20** on Cu(111) and Au(111) at room temperature proceed *via* initial loss of N_2 to give polymeric metallocarbene intermediates which in turn collapse to poly-α,β-unsaturated 1,4-diketones **21** (Scheme 12). On Au(111), these initial two steps proceed in sequence at room temperature, but for Cu(111) the second step occurs only at elevated temperature. Annealing of this material at high temperature gives 1,4-diketone cyclization to give polymeric structures linked by furan-2,5-diyl groups **22**.

The accessibility of *N*-heterocyclic carbenes (which are of course not necessarily derived from diazo precursors) and their excellent capability as ligands for metals is now being exploited in materials science,[86] particularly for the surface modification of nanoparticles, and found to be especially effective for gold[87-95] and copper for the introduction of superhydrophobic surface.[96] A report of the formation of polymethylene polymer films on gold has appeared.[97] A study of the binding modes of alkyl side chain substituted NHCs on gold have shown that short alkyl groups are up-standing, while longer alkyl groups lie flat with one Au binding two NHC ligands.[98] A review of the role of carbenes leading to the formation of alkylidene metals and their surface chemistry has appeared;[99] this has been used for the introduction of perfluorophenyl polymer brushes onto a gold surface.[100] The binding behaviour of several substituted methylenes (CCl_2, CFCl, CF_2 and CHF) on a Pd(110) surface has been studied using *ab initio* periodic DFT.[101] The modification of monolayer arsenic with dichlorocarbene has been examined; this occurs with high surface coverage and the introduction of luminescence.[102] Quantum-mechanical calculations using the density-functional-theory approach have been used to probe the properties of diamondoids after modification with substituted imidazolylidene ($C_3N_2H_6$) carbene **23** (R = $C_{10}H_{15}$, $C_{14}H_{19}$, $C_{18}H_{23}$, $C_{22}H_{27}$).[103] The addition of carbenes to single-walled carbon nanotubes (SWNT) has been investigated in detail, and found that not all reaction modes are equally favoured.[104]

Conclusion

The ready accessibility of diazo and diazonium compounds, and their capacity for collapse to reactive carbene or radical species with loss of nitrogen gas under benign conditions, or reaction by direct diazonium coupling, has allowed their application to the surface modification of diverse materials and for the introduction of a wide range of properties. Although the precise nature of the newly formed bonding nor the mechanism of its formation at the surface is not always clear, and that both monolayer and multilayer formation is possible, the lack of reaction selectivity is precisely what gives the methodology its wide scope and therefore value. The generality, versatility and convenience of their reactivity fits all of the key criteria proposed by Sharpless *et al.*[3] for the definition of a "Click Reaction" and, on this basis, diazo and diazonium coupling process may be appropriately thought of as "Surface Click Reactions" offering the opportunity for modification of surface chemical functionality in diverse substrates but without alteration of the bulk material. Their tolerance of ambient and biologically relevant conditions (oxygen, water) means that opportunities for wide application are likely to emerge; applications as efficient bioadhesives are an interesting example.[105-107]

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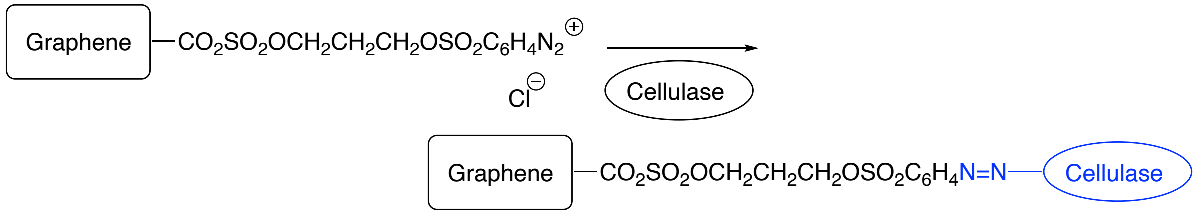
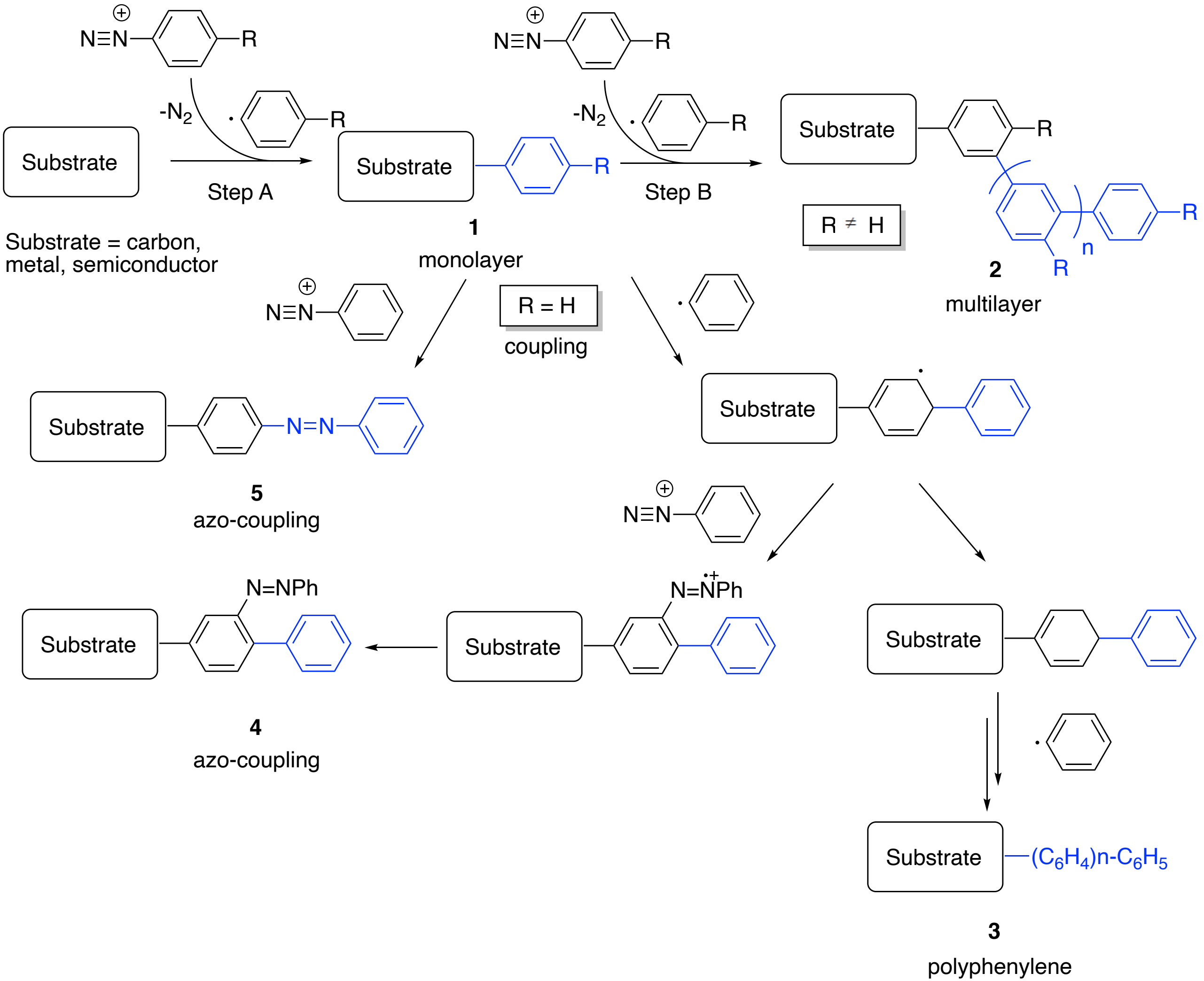


Scheme 1



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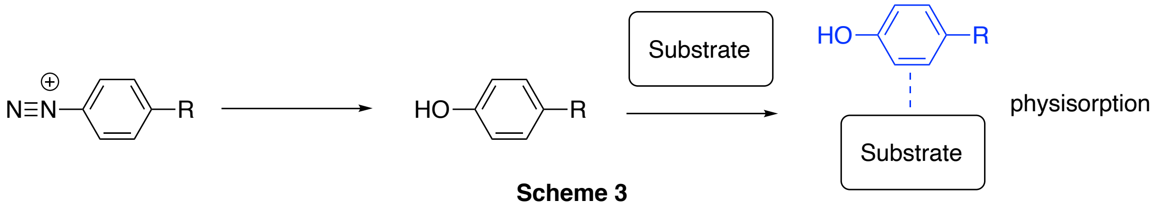

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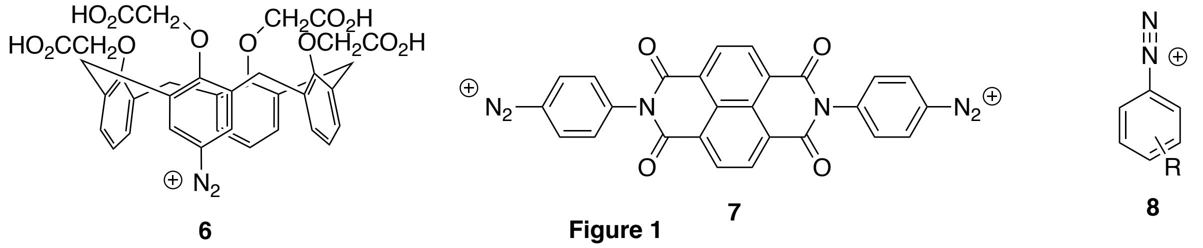

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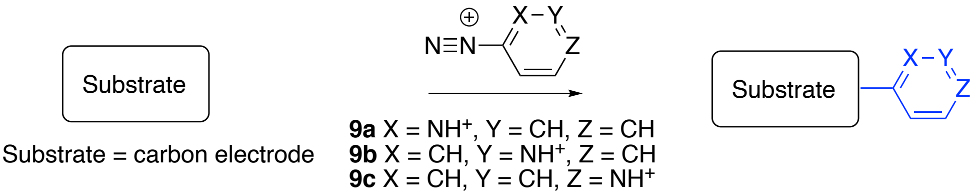
Figure 1



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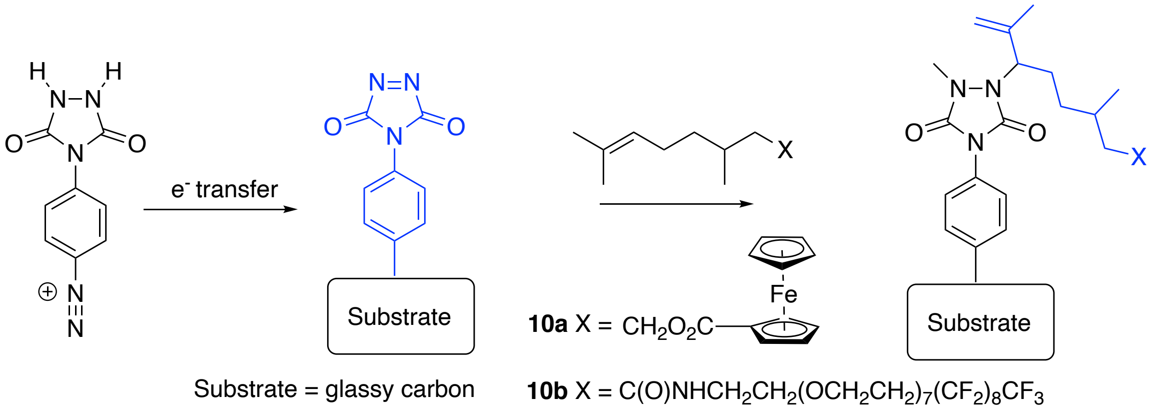

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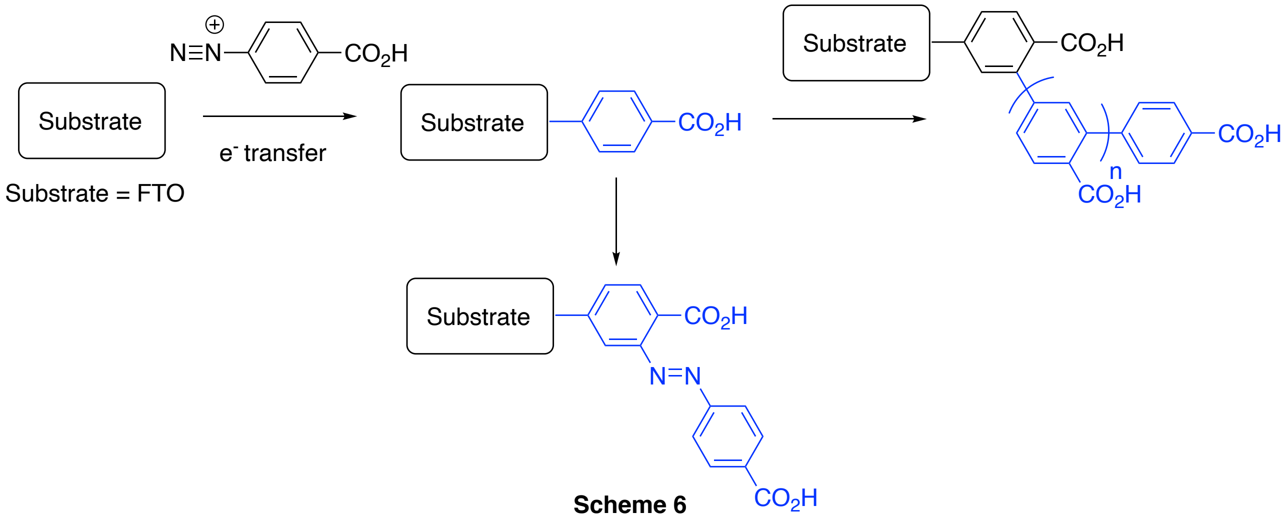

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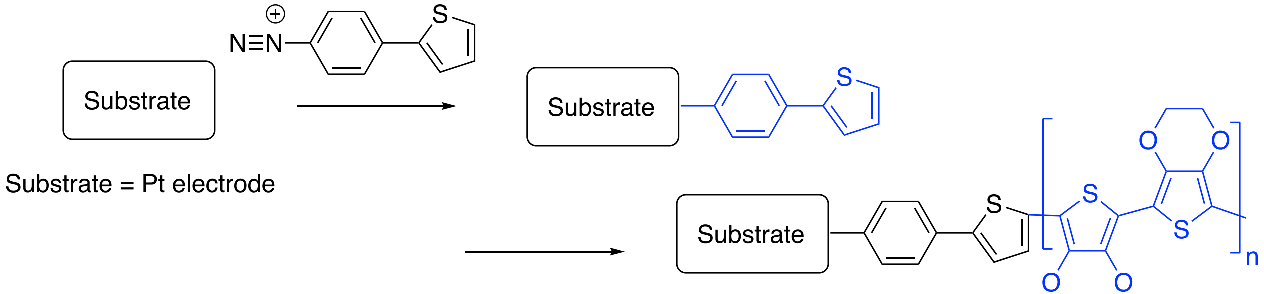

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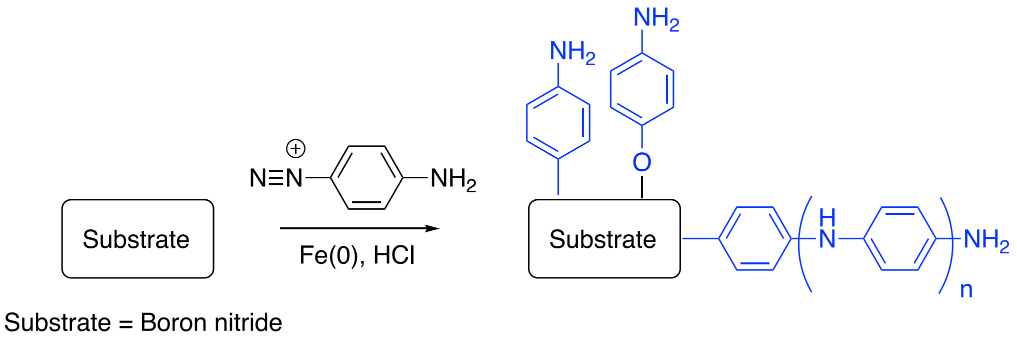

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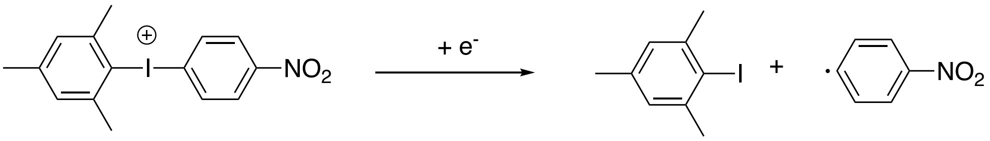


Scheme 9

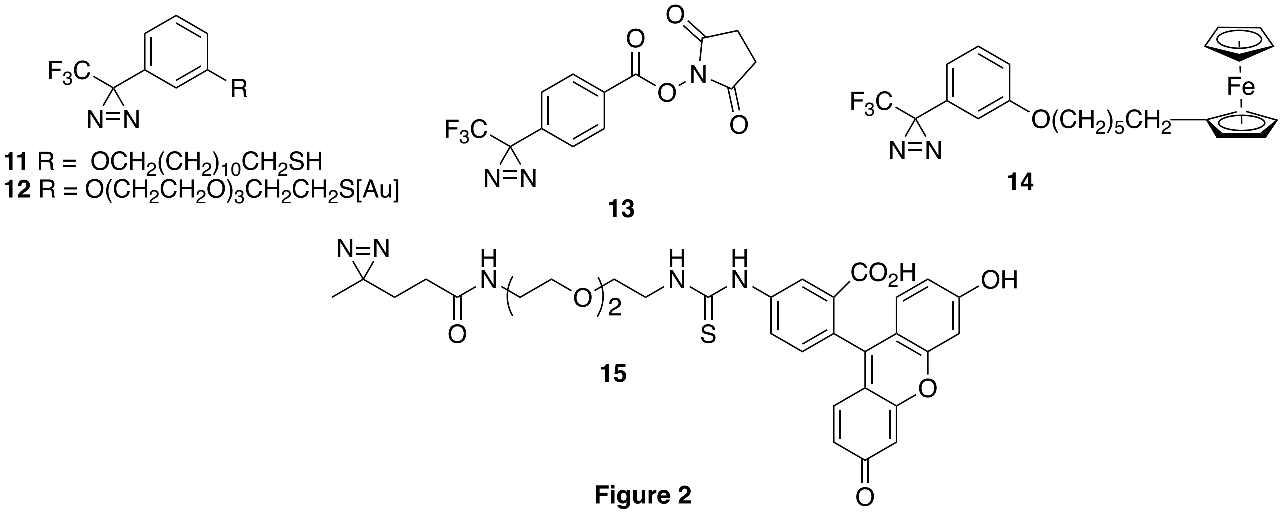
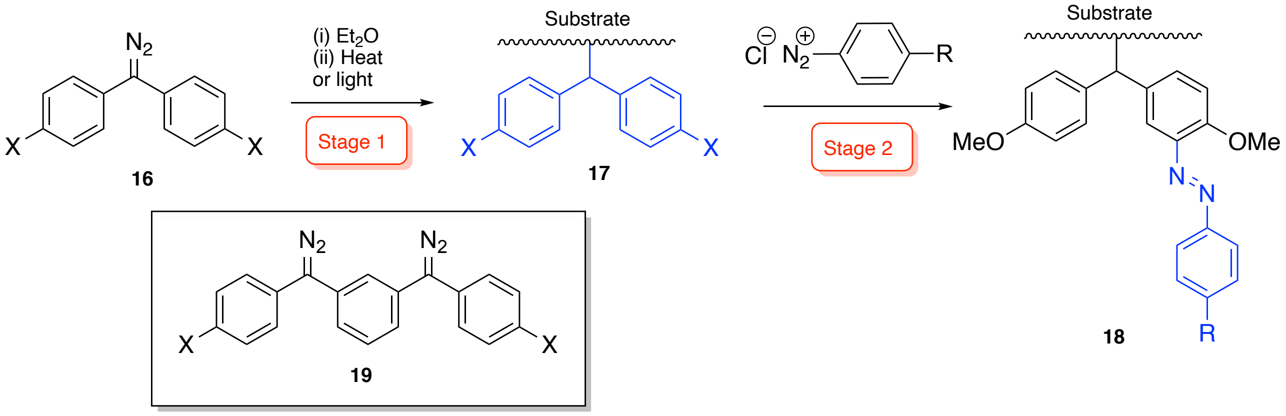
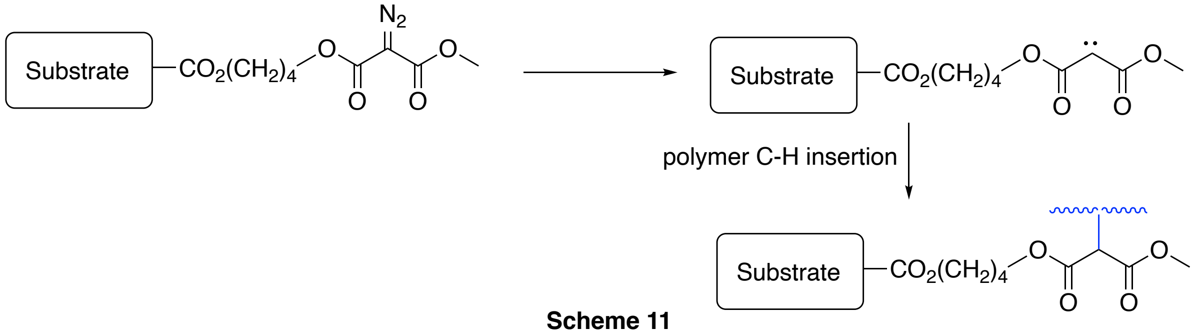


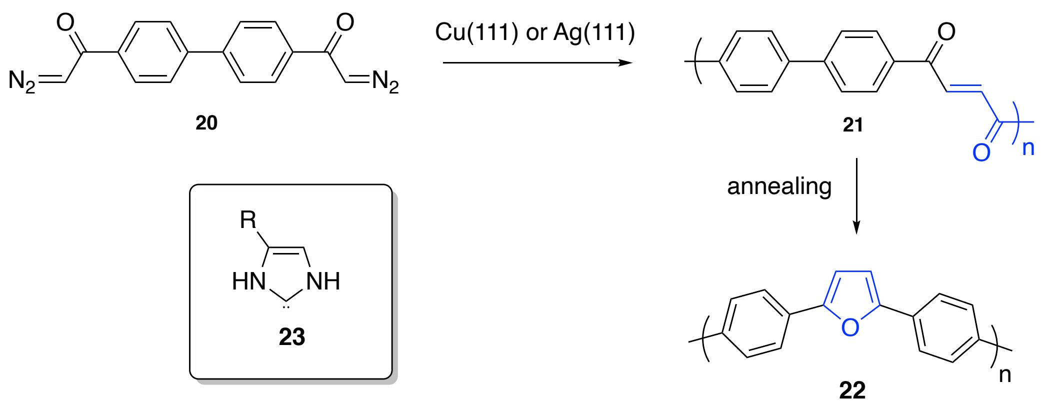
Figure 2



Scheme 10



Scheme 11



Scheme 12