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Review

Linkers for anchoring sensitizers to semiconductor nanoparticles

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Contents

Abstract

Organic and inorganic dyes anchored to semiconductor nanoparticles find important applications as photosensitizers in the preparation of solar cells and other optoelectronic systems. For many years research in this area has involved dyes that are bound to the surface of nanocrystalline semiconductors through one or more anchoring groups, forming donor–acceptor systems where the donor is usually the dye and the acceptor is the semiconductor. The design of linkers containing a bridge between the chromophore and the binding group is a more recent development in this field. Carefully designed linkers can be useful to fix the distance of the dye from the semiconductor surface, to tune the properties of the dye, to prevent aggregation of the chromophores, and to prepare models for interfacial electron transfer studies. More generally, this appears to be a promising method for understanding electron transfer processes at the molecule–nanoparticle interface and eventually controlling them in a rational and predictable manner. This review describes the synthesis and properties of sensitizers consisting of chromophore-linkers arrays where the linkers are based on alkyl chains, rigid-rods, or tripod-shaped molecules.

Keywords: Linkers; Sensitizers; Semiconductor nanoparticles; Photovoltaics

1. Introduction

Since the early 1970s, mesoporous anatase TiO_2 thin films coated with dyes find use as photoanodes of photoelectrochemical cells for solar energy conversion [1]. When the dye-coated film is the anode in a solar cell, photoexcitation of the dye (sensitizer) with visible light is followed by injection of an electron in the conduction band of the semiconductor. These are the first steps in a series of electron-transfer processes that ultimately result in the production of electrical energy from light. Fig. 1 shows this cycle for a cell sensitized by a Ru-polypyridine dye. Ultrafast laser techniques have shown that injection times for a variety of anchored sensitizers are in the range of few tenths to several hundreds of femtoseconds [2–5] while the recombination (a competing process) is several orders of magnitude slower. Interest in this field has exponentially increased in the last decade, since Grätzel and coworkers produced the first cells with substantially higher conversion efficiencies by using sol–gel techniques to manufacture films with enormous surface area for the dye uptake [6,7]. This finding demonstrated that dye-sensitized cells are a viable alternative for existing

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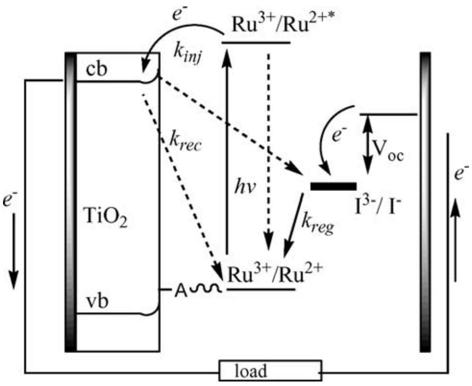


Fig. 1. Key electronic processes in a solar cell sensitized with a Ru(II)-polypyridyl dye anchored through A: $h\nu$, photoexcitation of the dye and formation of the lowest excited state, a metal-to-ligand charge-transfer (MLCT) transition; k_{inj}, electron injection, k_{rec}, recombination; k_{reg}, reduction of Ru(III) by the redox mediator (dye regeneration). Dotted arrows indicate competing processes.

solar cells technologies. Indeed, the recent generation of Grätzel cells, prepared from $\mathrm{Ru(L)(NCS)_2}$ sensitizers, can reach efficiencies close to 12% [1a,8].

The sensitization of wide band gap semiconductors finds numerous other applications in the preparation of photochromic and electrochromic devices, in photographic and xerographic processes, displays, and artificial photosynthetic centers [1a]. Given the fundamental and practical importance of this complex interfacial process, many research groups worldwide are involved in the effort to understand and control the sensitization events. Virtually each component and process of dye–semiconductor systems—the semiconductor [1c,9], the dyes [1a,10], the mechanism of injection and recombination [1b,1d,1e,11] have been extensively investigated. Directions of future areas of research and applications have been outlined [12].

This review focuses on a relatively new topic in this field: the design of linkers that anchor the dye to the surface of the semiconductor to form sensitizer-bridge-anchor arrays as represented in Fig. 2. The most common sensitizers for thin film electrodes are metal complexes of polypyridines [13], because they strongly absorb in the visible, have long excited states lifetimes, exist in stable oxidized and reduced forms, and do not have the tendency to aggregate or degrade. Their photophysical and electrochemical properties can be finely tuned by varying the metals and the ligands. Numerous other dyes including porphyrins [14], phthalocyanines [15], viologens [16], Rhodamine B [17] and xanthene dyes [18] have been employed. Perylene [2a,2b], naphthalene [19] and other organic aromatic hydrocarbons [20] have been used in fundamental studies aimed at elucidating the interfacial electron transfer events.

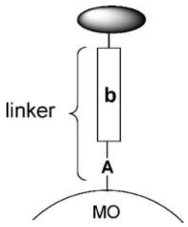


Fig. 2. Schematic representation of linkers used to bind sensitizers to metal oxide (MO) nanoparticle surfaces: **S**, sensitizer; **b**, bridge; **A**, anchoring group(s).

In early experiments, the dye molecules were adsorbed on semiconductor films by physisorption. This was done by dipping the films cast on a substrate, for instance a conductive glass slide, in a solution of the dye and then drying them in air. It was soon obvious that it was important to develop better methods to control the binding process, and already in the 1970s researchers were preparing dyes with anchoring groups that could bind covalently to semiconductor surfaces [21]. This expedient led to substantially improved sensitized films with higher surface coverages, increased stability, minimal desorption, and with a more even distribution of the dyes to form monolayer coverages. Most importantly, the covalent bond increases the strength of the electronic coupling between the molecular orbital of the dye and the semiconductor levels, leading to fast injection rates [1b]. For these reasons, most studies today involve sensitizers substituted with anchoring groups, such as phosphonates or carboxylic acid derivatives, that form strong bonds with metal oxide nanoparticles. The anchoring groups are often directly attached on the molecule's framework, as shown in Fig. 2.

The design of rigid linkers that spatially separate the dye from the semiconductor with a bridge is a relatively recent development, although dyes attached through flexible alkyl chains have been known for years (Fig. 3). The strategy of separating an electron donor and an electron acceptor with a bridge is well established. Donor–bridge–acceptor compounds made of two chromophores that are connected by saturated, unsaturated, rigid or flexible bridges have been used by many groups worldwide to elucidate fundamental aspects of electron transfer theory in fluid solutions, and as models to mimic electron transfer events in biological systems, Fig. 4a [22]. As for interfacial donor–bridge–acceptor systems, self-assembled monolayers (SAMs) made of thiols capped with electroactive groups and bound to gold electrodes through rigid or flexible bridges have been investigated for many years, Fig. 4b [23]. Donor–bridge–acceptor systems are finding increasing applications in the functionalization of Au nanoparticles and CdS quantum dots, Fig. 4c: alkyl thiols are used as stabilizers and/or as surface modifiers and the linkers are often modified to incorporate groups that have useful functions [24].

A possible explanation as why there are still few examples of this strategy for semiconductor sensitization is that the introduction of longer bridges in this case seems counterproductive. For instance, in the case of thiols bound to gold the long saturated chains are necessary to form high quality SAMs. In the case of $\mathrm{TiO_2}$ nanoparticles, instead, a saturated bridge between the chromophore and the binding group

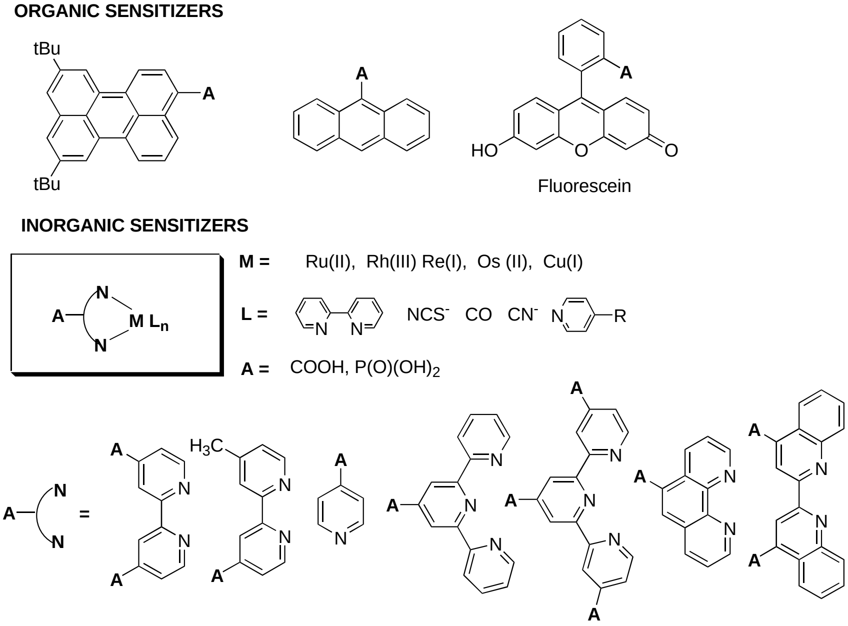


Fig. 3. Examples of organic dyes and components of metal complexes used for semiconductors sensitization in which the anchoring groups (**A**) are directly attached on the molecule's framework.

weakens the electronic coupling and slows electron injection rates, ultimately defying the purpose of anchoring the dye through covalent bonds. Injection through long linkers, however, can be rapid and efficient. For example, the lifetime of the MLCT state in Ru(II)-polypyridine dyes is usually several hundreds of nanoseconds, so that injections as slow as 1–10 ns can still occur with quantum yields near unity [1b]. Most importantly, it is now clear that well-designed linkers are highly useful in fundamental as well as applied research areas involving chromophore–semiconductor interfaces:

(a) *Organic linkers can be model compounds for mechanistic studies*. A better understanding of the electron injection and recombination dynamics at dye/semiconductor interfaces is the prerequisite for the improvement of solar energy conversion devices. Important theoretical and experimental progress has been reported in recent years, but many aspects remain unknown or are controversial. Hence, the importance to have well-designed models available. For example, "designer linkers" are being developed by several groups to study bridge mediated ultrafast heterogeneous electron transfer, to determine the distance dependence of electron transfer at the interface of semiconductors and whether it is appropriate to use the Marcus theory, and to understand if the injection can occur from vibrationally non-relaxed excited states.

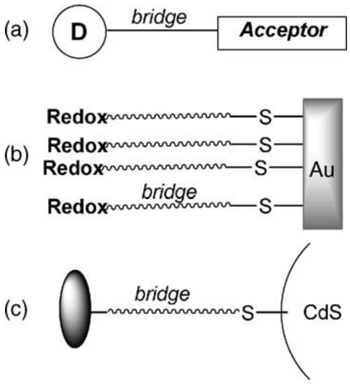


Fig. 4. General representation of donor–bridge–acceptor systems in solution and at the interfaces of gold and quantum dots.

(b) *Systematic length variation in rigid bridges can control the distance of the dye from the semiconductor surface*. The possibility of systematically varying the distance and orientation of a sensitizer from the surface with bridges of various lengths is useful for distance dependence studies and other applications. For instance, it may be possible to identify conditions where the excited state injection yield into the semiconductor is unity while recombination of the injected electron with the oxidized dye is inhibited. This is interesting because slower charge recombination rates are expected to increase the open circuit photovoltage, V_{oc}, which defines the maximum Gibbs free energy that a regenerative solar cell can produce under conditions of constant irradiance [25].

(c) *Linkers with large footprints can prevent dye aggregation*. Aggregation of the chromophores in their ground or excited state, especially at high surface coverages, is a recurrent problem in the case of dyes such as aromatic hydrocarbons, phthalocyanines and porphyrins and it has severely limited the use of these dyes. Excimers or dimers can have different electronic levels from the monomer, and aggregation can lead to excited state-ground state interactions. Chromophoric groups could be distanced from one another by using linkers with large footprints, a method that it is likely to be more effective than introducing bulky groups on the dye or adding co-binders (vide infra).

(d) *Bridges varying in structure and degree of saturation can tune the properties of the chromophore*. Highly conjugated bridges modify the properties of the dyes to which they are attached, and this strategy could be used to shift the absorption spectrum of organic aromatic chromophores to the visible and to increase their extinction coefficients. Also, such bridges could be used to tune electronic interactions between the chromophore and the semiconductor, raising the possibility of using them as “molecular wires” [26].

(e) *Linkers can be used for chemical surface modification*. Self-assembling multilayer techniques have been widely and successfully applied for the functionalization of electrodes, glass, metal surfaces and quantum dots, but there are fewer examples for TiO_2 nanoparticles [27]. This method is interesting because it may be possible, for instance, to graft a variety of redox or photoactive species to metal oxides such as ITO or TiO_2 previously modified with a linker that is capped with a reactive functional group, forming structurally well-defined arrays of photo or redox active molecules.

2. Organic linkers

This review focuses on recent developments towards the design of dye molecules that are covalently bound to metal oxides through organic linkers that are “non-chromophoric”. Therefore, we have not included bi- or multinuclear metal complexes, where the linker consists of one or more metal complexes linked together and where the bridge is specifically designed to participate in stepwise injection processes [28,13b]. Also, we have limited our horizon to molecular, non-polymeric, non-dendritic structures [29]. Since the terms bridge, spacer and linker are often used as synonyms, for clarity we call bridge (**b**) the moiety placed between the anchoring (or binding) groups (**A**) and the sensitizer (**S**), and linker the molecule that binds the dye and that contains both the bridge and the anchoring group(s), as shown in Fig. 2. While this is useful for classification purposes and to define the boundaries of this review, a net distinction between the various components is not always possible in the case of highly conjugated molecules. The designation “non-chromophoric” is clearly not appropriate in these cases.

2.1. The anchoring group

It is useful to summarize what kind of anchoring groups are used most frequently. Typically the best anchoring groups for metal oxides are phosphonic acids ($P(O)(OH)_2$) followed by carboxylic acids (COOH) and their derivatives, such as esters, acid chlorides, carboxylate salts, or amides [1a,30]. Silanes (SiX_3), ethers, acetylacetonate and salicylates have also been employed [30b]. They all form bonds with metal oxides by reacting with surface hydroxyl groups. In the case of phosphonates and carboxylates the binding is reversible with high equilibrium binding constants ($K \sim 1 \times 10^5\,M^{-1}$ for Ru-polypyridyne complexes attached through COOH groups) [31], and saturation surface coverages are in the range of $\Gamma \sim 1 \times 10^{-10}\,mol\,cm^{-2}$ [30b]. The dyes are easily desorbed from the films in basic conditions (usually pH $\geq$ 9). It has been shown that chemisorption at TiO_2 though COOH groups can occur though a variety of binding modes (Fig. 5) and which one is prevalent depends on the structure of the dye, the binding groups, the pH, and the semiconductor preparation [32].

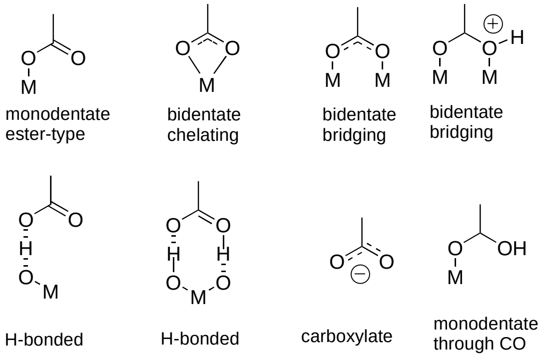


Fig. 5. Possible binding modes of a COOH group to a metal oxide (TiO_2).

The knowledge of the nature of the binding modes and of the binding geometry is crucial for the study of interfacial injection processes, to improve the electrochemical devices, and to design new sensitizers. The characterization of the binding is generally obtained by IR and Raman spectroscopy [33,31], XPS [34] and other methods [35]. However, given the complexity of the interface and the variables involved (adsorbed ions, surface geometry, etc. . . .), it is not always possible to determine all aspects of this interactions exclusively by experimental techniques, especially in the case of linkers that are large or have multiple anchoring groups. Quantum chemical calculations of model systems bound on rutile (1 1 0) and anatase (1 0 1) surfaces provide an important method to determine the more stable binding modes, to model the geometry of attachment and to study electronic properties of the interface [36]. For example, Persson et al. have developed quantum chemical INDO calculations for this purpose and applied their method to model the adsorption of bpy ligands on anatase (1 0 1) and to study the charge transfer excitation between the π-HOMO orbital of a bound catechol and the Ti(3d) levels at the bottom of the TiO_2 conduction band [36b]. Computational method like this will prove very useful to characterize the binding of many of the linkers described below and to design improved systems.

In the context of linkers, a thorough characterization of the binding is important for two additional reasons. First, if a linker is specifically designed to fix the distance of the chromophore from the surface, it is necessary to determine whether all anchoring groups are bound and how they bind. For instance, in the case of a tripodal linker, the assumption that such a molecule is positioned more or less perpendicular to the surface is correct only when all three anchoring group are bound.

Second, it appears that structure and size of organic linkers can influence the binding constant and surface coverage. For instance, weaker binding has been observed in lipophilic rigid rod linkers [37] and in anthracene bound through a single CH_2 bridge [19]. Linkers with multiple anchoring groups, such as tripodal sensitizers have exhibited instead binding constants that are one order of magnitude higher than those usually obtained for $Ru(bpy)_2(dcb)^{2+}$ [38]. Intuitively, one may expect that surface coverage will decrease when the linkers are bulkier or have a larger footprint, but many linkers described below are relatively new and this effect has been little investigated [39].

2.2. *Flexible or semirigid bridges*

Table 1 shows a list of linkers that employ flexible or semirigid bridges [2b,16a,40-52]. The first spacers used to anchor dyes to TiO_2 were synthesized as part of the effort to obtain more efficient cells by covalently attaching the dye to the thin film electrode. Often, the presence of a saturated bridge between the anchoring group and the dye was dictated by convenience and was a consequence of the functional groups interconversions used to prepare the anchoring groups. For instance, phosphonate groups can be prepared from bromomethylenic groups ($–CH_2Br$) by reaction with trimethylphosphite, resulting in phosphonomethyl derivatives ($–CH_2PO_3R_2$) [46]. Simple methods to prepare silylating groups involve hydrosilylation of vinyl groups or reaction of halides with (3-aminopropyl)triethoxysilane, and both methods introduce short alkyl chains ($(CH_2)_n SiR_3$) [41,47].

In other instances, the presence of even a single CH_2 bridging unit is part of a rational molecular design and originates from the idea of modifying the dye to probe the effect of a bridge on the electronic coupling [53] and, secondly, to provide a better defined reaction distance. For example, modified perylene chromophores have been specifically designed by Willig and coworkers [2a,2b,11h,44] to probe ultrafast interfacial photoinduced electron transfer kinetics in ultrahigh vacuum techniques. Bulky *tert*-butyl substituents were introduced on the perylene framework to prevent formation of dimers, and a single methylene bridge provided a reaction distance of three saturated bonds (Table 1, entry 9). Injection times were in the order of picoseconds, rather than femtoseconds. Their work demonstrated that electronic coupling can be greatly weakened by inserting a molecular spacer group with saturated bonds.

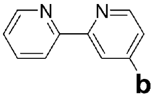
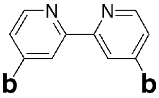
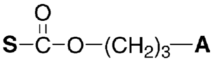
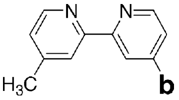
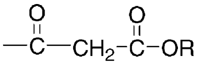
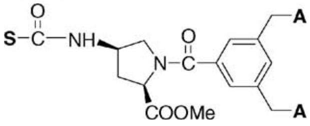
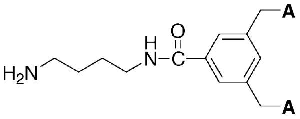
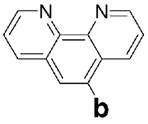
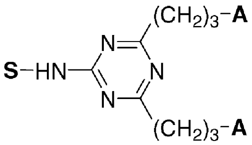
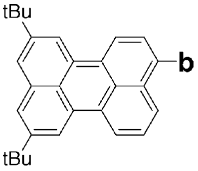
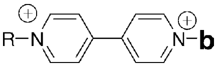
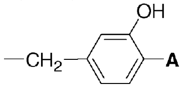
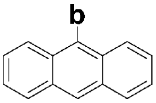
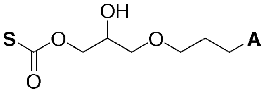
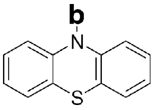
To study "long range" electron injection processes and to determine the effect of bridges, Meyer's group studied two Ru–polypyridyl complexes attached through propyl chains to TiO_2 thin films and made a comparison with the corresponding complex directly attached though the ligand (Table 1, entry 5) [45]. Their experiments showed that photocurrent efficiencies were the same for all three dyes and electron injection rates were beyond the detection limit of a nanosecond laser pulse ($>5 \times 10^8$). This observation demonstrated that intimate electronic coupling between the ligand and the surface link is not a strict requirement for fast injection. Interestingly, the recombination rate from TiO_2 to the oxidized dye was slower for the compounds with the saturated spacer and the differences between open circuit photovoltages (V_{oc}), although small, were consistent with the observed kinetics. This experiment also suggested that V_{oc} can be increased by using long linkers [25].

The use of variable length linkers for distance dependence studies has been recently explored by Lian and coworkers [42]. They inserted one to five methylenic spacers between the bpy ligand and the carboxylic group in $Re(CO)_3Cl(dcbpy)$ to form ReC1A–ReC5A, respectively (Table 1, entry 3). The complexes were bound to TiO_2 thin films and the dependence of electron injection dynamics on electronic coupling was studied by femtosecond IR spectroscopy. The injection rate decreased exponentially with distance, in qualitative agreement with the change predicted for nonadiabatic electron transfer processes. The injection from ReC0A, the dye that is directly attached to the surface, showed a <100 fs injection time, suggesting that electron transfer occurs in the strong coupling and adiabatic limit. The flexibility of the chain in the model compounds, however, does introduce uncertainty on the distance and orientation of the dyes with respect to the surfaces.

Hartland and coworkers compared 9-anthracene carboxylic acid (9-AC) and 9-anthraceneacetic acid (9-AA) attached to colloidal TiO_2 nanoparticles through a COOH and a CH_2COOH group, respectively [51]. While 9-AC/TiO_2 showed a red-shifted absorption spectrum and the fluorescence was quenched upon binding, 9-AA/TiO_2 showed no red shift and no fluorescence quenching. These data suggest that the presence of a single methylenic unit in 9-AA decreases the electronic coupling element by at least two orders of magnitude and that the electron injection time is longer than the lifetime of the excited state (~10 ns). The authors, however, were cautious in their interpretation as they had no definitive proof that 9-AA was bound to TiO_2.

An approach that results in the attachment through flexible linkers, but that involves a different concept, is the surface modification of the metal oxide and subsequent binding of the chromophoric groups [27a]. In a recent example, Ottenbrite's group has used 3-glycidoxypropyl trimethoxysilane (GPS), a silane coupling agent, for the surface modification of TiO_2 nanoparticles [48]. Rhodamine B and azo dyes where subsequently grafted onto the GPS modified particles. Meyer developed amino derivatives of diphosphonate anchors which were coupled to proline-substituted chromophores using a classical peptide coupling procedure [46].

Table 1
Examples of flexible linkers

Sensitizer or ligand (**S**)	Entry	Bridge (**b**)	Anchoring group (**A**)	MO_n	References
	1	$-CH_2-CH_2-$	$-SiCl_3$	SnO_2	[40]
	2	 $\mathbf{S}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-\mathbf{A}$ $-(CH_2)_n-$ n = 1-5 $-CH_2-$	$-SiCl_3$	SiO_2, ITO[a]	[41]
	3	$-(CH_2)_n-$ (n = 1–5)	–COOH	TiO_2	[42]
	4	$-(CH_2)-$	$-P(O)(OEt)_2$	TiO_2	[43]
	5	$-(CH_2)_3-$	 $-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OR$ —COOH	TiO_2	[45]
	6		$-P(O)(OH)_2$	TiO_2, ITO[a]	[46]
	7		$-P(O)(OH)_2$		[46]
	8		$-SiOEt_3$	SnO_2	[47]
	9	$-CH_2-$	$-P(O)(OH)_2$	TiO_2	[2b,44]
	10	$-(-CH_2)_2-$	$-P(O)(OH)_2$	TiO_2, SiO_2	[51]
		$-(-CH_2)_2-$	–COOH	ITO[a], ATO[b]	[16a,51]
	11		–COOH	TiO_2	[49]
	12	$-CH_2-$	–COOH	TiO_2, ZrO_2	[51]
Rhodamine B 4-phenylazophenol 4-phenylazoaniline	13		$-SiOEt_3$	TiO_2, SiO_2	[48]
	14	$-(CH_2)_2-$	–COOH	SiO_2, ITO[a], ATO[b]	[16,52]

[a] ITO: tin doped indium oxide, In_2O_3:Sn.

[b] ATO: antimony-doped tin oxide, SnO_2:Sb.

In principle the N-terminus of such linkers can be coupled with the C-terminus of peptide-capped chromophores either before or after binding to TiO_2. The increasing interest in TiO_2 nanoparticles surface modification is shown by studies of self-assembled monolayers, although in these cases the simple alkyl chains do not carry a chromophore [54].

2.3. Rigid linkers

The trend that has been observed in studies of dyes attached through flexible saturated linkers indicates that the electronic coupling is weakened by the introduction of one or more saturated methylenic bridges and that electron injection rates slow down with increased bridge length. Instead of discouraging the chemists from developing longer linkers, these observations have demonstrated the importance of having better synthetic models available. It became clear that studies aiming at determining fundamental aspects of the interfacial electron transfer processes require well-defined molecules for which parameters such as length of the linkers and degree of saturation of the bridge can be systematically varied. For example, in the case of distance dependence studies the distribution of possible conformations of the flexible linkers makes it impossible to accurately estimate the distance [42].

For these reasons, synthetic efforts in this area have been redirected towards the design and synthesis of linkers that are *rigid* [37,38,55]. Given the increased complexity of the final molecules, the synthetic approaches generally involve the use of components (i.e., the bridge, the chromophore, the footprint) that can be synthesized separately and then assembled together in a convergent approach [55]. From a synthetic point of view, most of the rigid linkers prepared to date are challenging to prepare. Also, rigid molecules are usually associated with poor solubility, although this problem has been solved by the temporary or permanent introduction of solubilizing groups. Finally, there is also the question of how linkers that are longer or bulkier can influence the surface coverage and binding properties. Overall, the work that is shown below has proven that the increased synthetic challenge is worthwhile and that the rigid models prepared are very useful. Because of the novelty of some systems it is important to emphasize that there is work in progress as this review is being written.

2.3.1. Rigid axial rods

Until about 15 years ago, there were few non-polymeric, covalently-linked, well-defined molecules having the shape of rigid-rods with axial (cylindrical) symmetry. Examples are shown in Fig. 6. The widespread interest in rigid-rod molecules during the past decade is mainly due to their role in the synthesis of models for electron transfer studies and their utility as building blocks for nanosized molecules and supramolecular assemblies. The need for rigid rods of various symmetry (axial, zig-zag- or ladder-shaped) and structure (saturated, unsaturated, metal-based), led the synthetic chemists to build a vast library of rod-shaped compounds over the last decade. A comprehensive classification of molecular rods, their syntheses and applications has been reviewed [56].

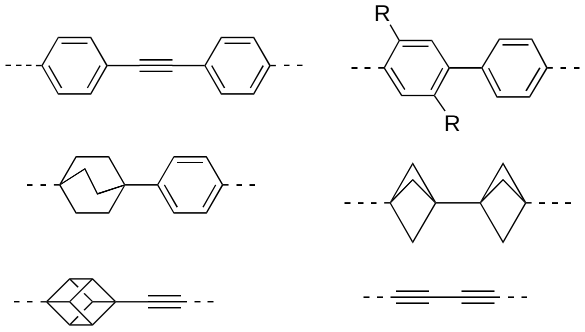


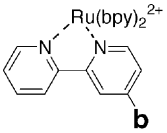
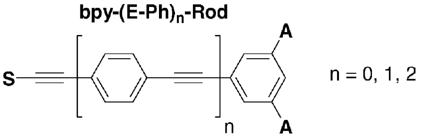
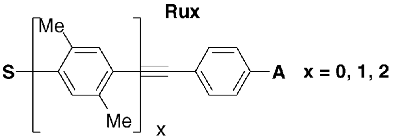
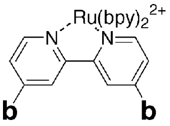
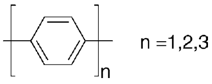
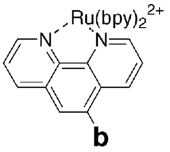
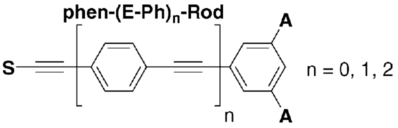
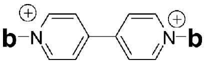
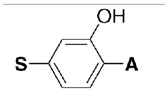
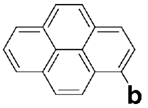
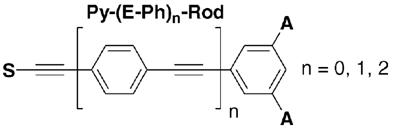
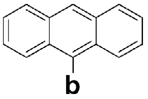
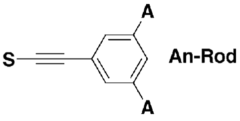
Fig. 6. Example of bridges that have the shape of rigid, axial rods.

From a synthetic point of view, the rigid rods that are most common and easiest to prepare are unsaturated rigid axial rods made of oligo-*p*-phenylenes and oligo-*p*-ethynylphenylenes. These are usually synthesized by iterative Pd-catalyzed cross-coupling, such as Sonogashira and Suzuki reactions [57]. These classical and widely used coupling methodologies involve synthetic procedures and catalysts that have been tested for many years, use building blocks that are commercially available or easily synthesized, and allow functionalization at the termini of the rods. Solubilizing groups can be introduced as alkyl substituents on the phenyl groups. Rigid rods prepared in this way have been used to separate bimetallic complexes of polypyridines, to build porphyrine arrays and as bridges between electron donors and acceptors for solution or surface studies [58]. More recently, nanosized conjugated axial rod oligomers have been investigated as “molecular wires” [26].

Examples of axial rods as linkers for nanoparticles sensitization, however, are scarce. Kalyanasundaram et al. prepared Ru complexes containing *p*-carboxyphenyl substituents in the 4,4′-position of the bpy ligand (DCPB complexes) with the aim of tuning the MLCT using peripheral π-acceptor substituents [59]. The observation that the charges were not delocalized through the phenyl bridges, however, accounted for the inefficient sensitization of the TiO_2 films by the DCPB complexes (Table 2).

Rigid linkers with a bridge for which the number of units can systematically be varied, as shown in Fig. 7, have been independently synthesized and studied only recently in two research groups. Lewis and coworkers have prepared *p*-xylene-based rods terminated with one carboxylate group and substituted with a Ru complex (Rux rods where $x = 0$, 1 and 2 xylyl groups) [60]. Galoppini has prepared rods made of phenylethynyl units terminating with two carboxylate anchoring groups and substituted with Ru-polypyridyl complexes as well as organic chromophores (S-(E-Ph)$_n$-Rods where S: sensitizer and Rod: dimethyl 4-ethynyl-isophthalate) [37,55b]. IR spectra of such rods

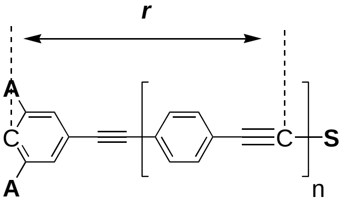
Table 2
Axial rigid-rod linkers

Chromophore (**S**)	Entry	Bridge (**b**)	Anchoring group (**A**)	MO_n	References
	1		–COOMe	TiO_2, ZrO_2	[55b]
	2		–COOH	TiO	[60]
	3		–COOH–	TiO_2	[59]
	4		–COOMe	TiO_2, ZrO_2	[55b]
	5		–COOH	TiO_2	[16a]
	6		–COOR, R = Me, H, Na	TiO_2, ZrO_2	[37,55b]
	7		–COOMe	TiO_2	[55b]

attached to TiO_2 thin films indicate that both COOR groups bind *via* an ester-linkage [37].

Both types of linkers, when capped with Ru-polypyridyl complexes, exhibited similar photophysical and photoelectrochemical behavior. In all cases, the PL decays in acetonitrile solutions followed single-exponential kinetics, as shown in Table 3. The charge recombination between the electrons in TiO_2 and the oxidized Ru(III) center exhibited multiexponential behavior, and the recovery of the ground state MLCT absorption in the Rux rods was fitted to a sum of two second order kinetic constants. The multiexponential behavior after binding is observed also in complexes that are directly anchored to the surface, such as $Ru(bpy)_2(dcb)^{2+}$, and has been ascribed to the heterogeneity of surface microenvironments at the binding site. For both classes of rods the shortest injection rates ($\sim 1 \times 10^8\ s^{-1}$) were close to the width of the instrument response function of a nanosecond laser (~10 ns). In the case of the Rux compounds, the dependence on the linker length was weak: a decrease of a factor of two as the Ru–COOH distance increased from 13.8 to 22.5 Å. Qualitatively, similar behavior has been observed for the Ru-(E-Ph)-Rods and famtosecond laser spectroscopy studies of these rods are in progress.

The fact that it has not been possible to establish a distance dependence for injection and recombination processes, and the observation of multiexponential kinetics for



n	C to C r(Å)
0	5.4
1	12.2
2	19.1

Fig. 7. Length of bridges in a rigid-rod linker. Adapted from [55b].

Table 3
Solution photophysical and electrochemical properties of selected rigid-rod sensitizers from Table 2 and of reference compounds[a]

Entry	Rod sensitizers from Table 2	$\lambda_{\max\,abs}$[b] (nm) (ε, $M^{-1}\,cm^{-1}$)	$\lambda_{\max\,ems}$[c] (nm)	ϕ_{ems}[d] (%)	τ_{ems}[e] (μs)	$E^{\circ}_{1/2}$ (V)[f]
1	Ru0[g]	467	648	9.7	2.1	1.36
2	Ru1[g]	453	621	7.5	1.06	1.34
3	Ru2[g]	455	621	7.1	1.04	1.33
4	Bpy-Rod[h]	462 (1.6×10^4)	640	11	1.9	1.30
5	Bpy-E-Ph-Rod[h]	465	640	13	2.6	1.30
6	$Ru(bpy)_3^{2+}$[h]	450	626		0.8	1.26
7	$Ru(Phen\text{-}E\text{-}bpy)_3^{2+}$[h]	468	605		1.1	1.43
8	Py-Rod[i]	383 (5.3×10^4)	425	0.33	3.1×10^{-3}	1.18
9	Py-E-Ph-Rod[i]	399 (8.2×10^4)	445	0.41	1.8×10^{-3}	1.15
10	Py-CO_2H[i]	351 (3.2×10^4)	390	0.34	10.1×10^{-3}	1.29
11	Pyrene[i]	335[g] (4.9×10^4)[j]	375, 395[k]	0.72	190×10^{-3}	1.16

[a] Measurements were performed in CH_3CN degassed with N_2 at room temperature.

[b] Absorption maximum, ±2 nm.

[c] Corrected singlet emission maximum, ±5 nm.

[d] Fluorescence quantum yield, ±5%.

[e] Excited state lifetime, ±2%.

[f] Formal reduction potentials reported vs. SCE as estimated from cyclic voltammetry data obtained by adding **1**–**3** dissolved in a minimal amount of CH_2Cl_2 to 0.1 M $TBAClO_4/CH_3CN$.

[g] From [60].

[h] From [55b].

[i] From [37].

[j] In EtOH.

[k] In CH_3CN.

both injection and recombination processes seem to point to a distribution of orientations, possibly due to variations in the angle of attachment of the carboxylate group the surface. Clearly, while the length of the bridge can be increased systematically, as indicated in Fig. 7, little is known about the geometry of the bound molecule with respect to the surface, and computational work done on small benzene derivatives bound to TiO_2 suggests that it is unlikely that the axis of the rod is perpendicular to the surface. This is also the case for the Rux rods, which have a single point of attachment. However, it is to be determined whether the multiexponential behavior is due to other effects (for instance it is not known whether axial rod linkers are indeed rigid on the ultrafast (famtosecond) timescale of the experiment). Photoelectrochemical solar cells prepared from the Rux rods exhibited rather low efficiencies, comparable to that of a Ru-bpy complex directly attached through one COOH group, and the current density (J_{sc}) decreased by about a factor of 2 for each incremental xylyl unit [60]. The observation that an increase in length decreases the cells efficiency, in this case seems to be due to competing electron transfer from the TiO_2 to the redox mediator.

The presence of π-acceptor groups on the ligands has an effect on the absorption and photoluminescence and transient absorption spectra of the resulting Ru complexes, particularly in the case of the S-(E-Ph)-Rods where a coplanar conformation of the benzene rings in the phenylethynyl bridges is energetically stable [37]. Structurally, the Ru-(E-Ph)-Rods are similar to the Ru complexes carrying a bpy ligand substituted with oligomeric phenylethynyl units in the 4,4′-positions (4,4′-bpy-PE), which have been studied by Schanze and coworkers to determine substituent effects in oligo- and polymeric π-conjugated Ru-polypyridyne complexes [58,61c]. All photophysical data in the Ru-(E-Ph)-Rods and in Schanze's complexes indicate that the MLCT is localized on the 4,4′-bpy-PE ligand, and electrochemical and computational data indicate that the LUMO energy of that ligand is lowered, although it is less clear to what extent the excited electron is delocalized into the phenylethynyl bridges. In both cases, the absorption data did not exhibit further significant red-shifting as the number of the phenylethynyl units increased.

A promising development that takes advantage of the π-conjugated bridge is the use of linkers to tune the photophysical properties of a chromophore attached to the linker. For instance, Meyer and Galoppini have shown that the presence of fully conjugated rods increases the extinction coefficient of an attached pyrene and shifts the long-wavelength absorbance of pyrene to the red, as shown in Fig. 8 [37]. In addition, the pyrene rods were used to prepare efficient and stable regenerative solar cells with absorbed photon-to-current efficiencies close to unity. These results suggest that highly conjugated rods may be useful linkers for enhancing the efficiency of an otherwise unsuitable chromophore by shifting its spectrum to longer wavelengths of light.

2.3.2. *Tripodal linkers*

The use of a tripodal surface linker (termed "spider", shown below) was first reported by Whitesell and coworkers [62]. Three-armed thiols based on trialkylmethylamines were capped with fluorescent or redox-active molecules

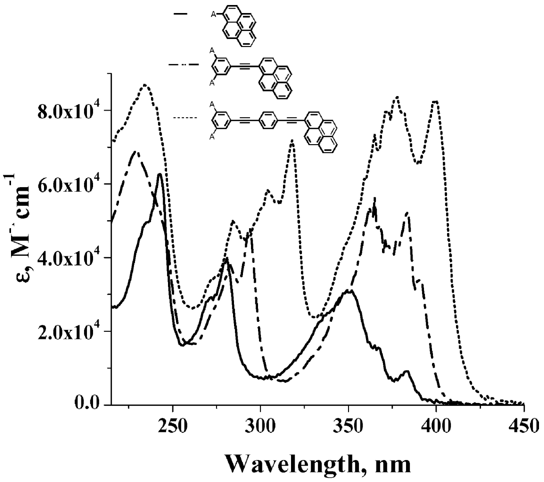
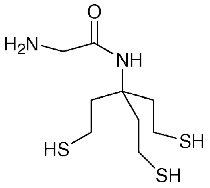


Fig. 8. Absorption spectra of pyrene-substituted rods in acetonitrile: **A**, COOMe. Adapted from [37].

through polypeptide bridges to form SAMs on gold and, more recently, to anchor antibodies to colloidal metal particles for biological cell separations [63].



Experimental evidence indicated that the "spiders" like the one shown below were holding the end-groups almost perpendicularly to the surface. This design has been adopted by others for binding molecules to gold. Tripod-shaped thiols having an oligothiophene arm linked to redox active groups, such as fullerene, have been used to prepare SAMs on gold electrodes for chemical sensors and organic light emitting diodes (OLEDs) [64–67]. Moreover, Tour has synthesized silane "caltrops" with very large thiol-terminated arms for atomic force microscopy applications [67].

Galoppini and coworkers have developed rigid tripodal linkers that anchor to semiconductor nanoparticles [38,55b,68-70]. Tripodal linkers having three points of attachment and a fourth rigid arm that carries the chromophore were made from 1,3,5,7-tetraphenyladamantane (Ad-Tripods) tetraphenylmethane (C-Tripods) and, more recently, Si derivatives (Si-Tripods), Fig. 9. The tripods were substituted with Ru-polypyridyl complexes and other organic chromophores. This design is clearly better than the axial-rod to control distance and binding geometry because tripods stand perpendicularly on the oxide surface when all three anchoring groups are bound. The length of the arm carrying the sensitizer can be varied.

The study of tripodal linkers capped with Ru-polypyridyl complexes has shown that all three COOR groups are bound, that the spectral properties are unchanged upon binding (suggesting weak coupling to the semiconductor), and that the MLCT state is always localized on the tripodal linker, not on the auxiliary ligands, when the auxiliary ligands are unsubstituted bpy. More recently, these tripods have been used as models to study long range interfacial charge injection over a distance of ∼24 Å [68]. Piotrowiak and coworkers performed a photophysical study of **2** and **3** (Fig. 10a) bound to TiO_2 mesoporous films, with **1** as the reference [68]. The structures of **2** and **3** are identical except for the ligand connecting the Ru(II) center to the tripod (phenanthroline in **2** and bipyridine in **3**).

For the reference complex **1**/TiO_2, consistent with the reports of other groups [2,3], the electron injection occurred within the instrument response time (∼100 fs). Fig. 10b, lowest trace, shows the long-lived absorption of the electron in TiO_2 following photoexcitation of **1**/TiO_2. The kinetics for **2** and **3** were fit using bi-exponential decays, Fig. 10b, with **2** injecting faster than **3**. In both cases, there was a slow ($\tau \sim 3$ ps) component ascribed to the long range injection, together with a remarkably fast sub-picosecond component (240 fs (67%) for **2** and 450 fs (35%) for **3**), Fig. 10b. The ultrafast component can be rationalized considering the extensive π-conjugation of the bridge. The faster injection exhibited by the phen-based **2** can be explained by the fact that the LUMO electron density at the C5 bridging carbon atom of the phenanthroline in **2** ($C5\rho_{LUMO} = 0.15$) is much larger than that at the corresponding C4 bridging carbon atom of the bipyridine in **3** ($C4\rho_{LUMO} = 0.02$). This suggests stronger electronic coupling between the phenanthroline

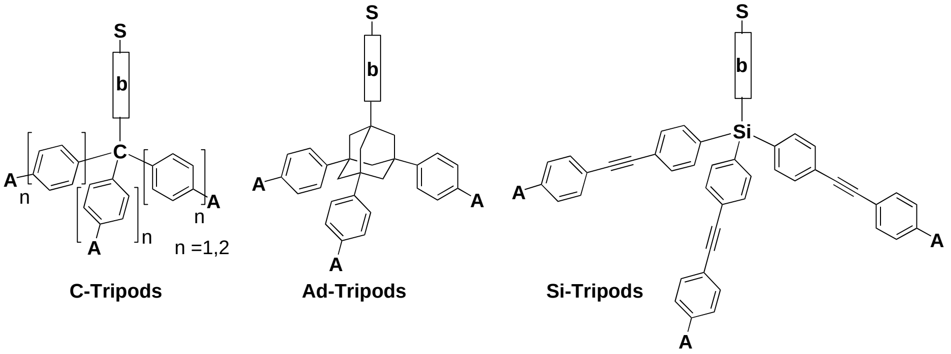


Fig. 9. Tripodal linkers for semiconductor nanoparticle sensitization.

fragment and the conjugated bis-phenylethynyl bridge. The authors propose that the ultrafast component could be due to “hot injection”, i.e. charge injection proceeding prior to full thermalization of the excited state. The detection and study of this event is of important for the field of photovoltaics [1e,2]. Clearly, while this behavior is still being studied and the possibility of other processes such as injection on adjacent nanoparticles has not yet been excluded, the long tripods are very promising model compounds.

The tripodal linker strategy is now being applied to study other sensitizers, such as viologens [71] and porphyrins [72]. Fitzmaurice and coworkers have applied the tripodal linker strategy to attach viologen to the surface of TiO_2 nanoparticles [71]. These 1,1′-disubstituted 4,4′-bipyridinium salts exhibit reversible electrochemical behavior in solution, are good electron acceptors ($E_0 = -56$ V) and for these reasons have been used as quenchers for Ru(II) complexes, to study lateral electron and energy transfer between donors and acceptors bound to semiconductors, and for the preparation of colored electrochromic windows [16]. Because of the perpendicular binding geometry, the polyether substituent on the viologen is able to thread a crown ether and form a rotaxane-type complex.

Galoppini and coworkers have prepared tripods with large footprints to investigate whether this can prevent aggregation phenomena, including excimer formation, that are typically observed with organic aromatic dyes. The strategies employed to date have involved the use of bulky groups, for instance the *tert*-butyl substituents on Willig’s perylenes [44], or the use of bulky co-binders such as chenodeoxycholic acid [15], to “dilute” the chromophores on the surface. Tour’s caltrops synthesis [67] was adapted to synthesize a Si-Tripod terminated with a pyrene chromophore, having a large footprint (~190 Å^2) to prevent excimer formation [70].

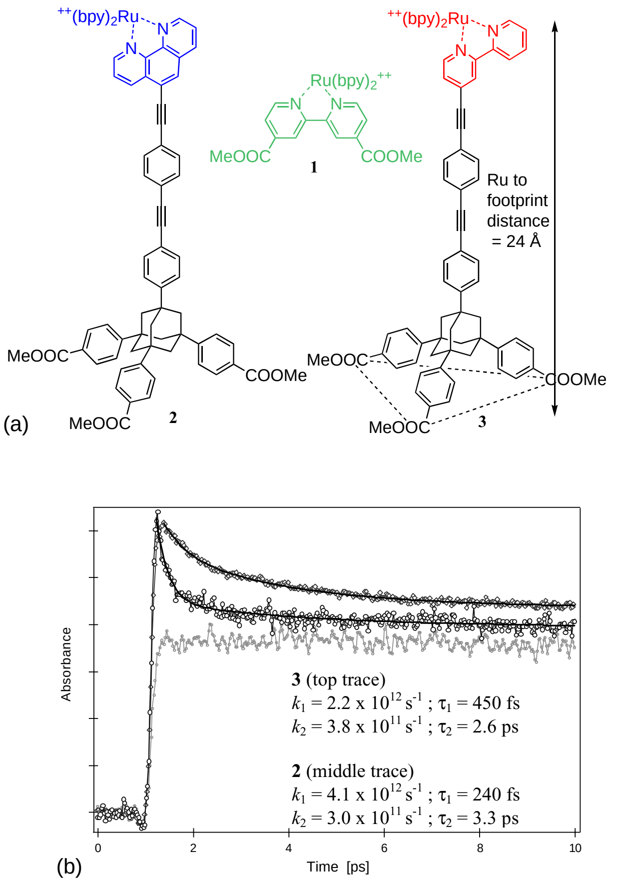


Fig. 10. (a) Structure of Ad-Tripodal sensitizers **2** and **3** and reference complex **1**. (b) Kinetic traces for **1**/TiO_2 (bottom), **2**/TiO_2 (middle) and **3**/TiO_2 (top) systems excited at 405 nm and monitored at 900 nm. Pulse length ~110 fs. The bi-exponential fits are shown by the solid lines. For **1**/TiO_2: $k_{inj} > 1 \times 10^{13}$ s^{-1}. Adapted from [68].

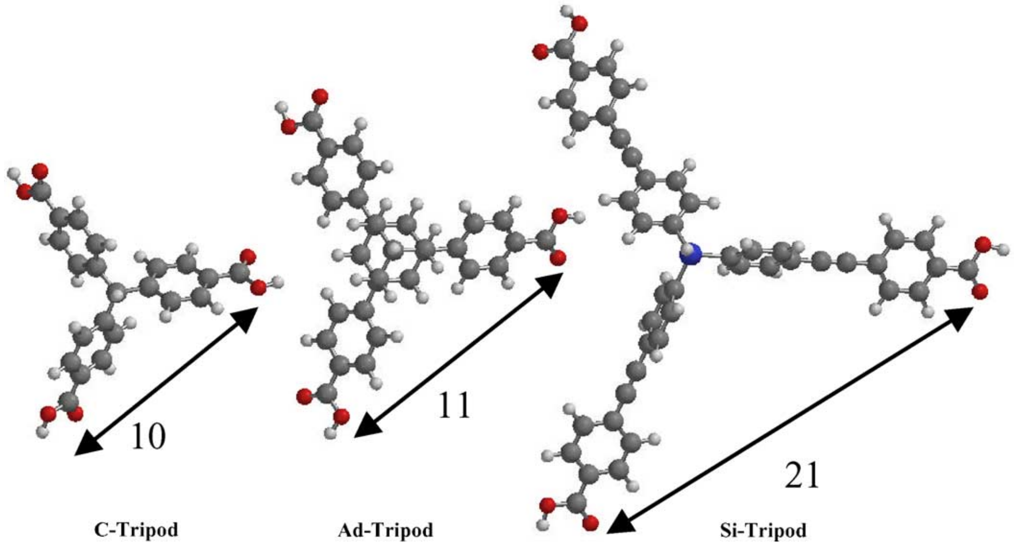


Fig. 11. Comparison of footprints of three tripodal linkers with different cores. Models derived from semi-empirical calculations. The O–O distances are subject to small changes, depending on the rotation of the COOR group.

Fig. 11 shows a comparison between the footprints of the various tripods.

2.4. Other systems

Finally, the extent to which semiconductor surface modification has developed and the importance of the molecular design of the sensitizer are well illustrated by the two examples of linkers shown in Fig. 12. These were not included in the tables because in both cases the linker is a chromophore and participates in the electronic processes.

Walder and coworkers have studied the electrochromic properties of mono-, di- and trimeric viologen derivatives bound to TiO_2 electrodes through benzoate, salicylate and phosphonate anchoring groups [73]. The shapes of the molecules, which have nm-scale lengths and are therefore comparable in size to a TiO_2 nanoparticle, were carefully planned. For example, the cone-shaped alborol derivative shown in Fig. 12a was designed to improve the coverage of the convex nanoparticle surface by fitting together like wedges, and a trimeric viologen with three anchoring

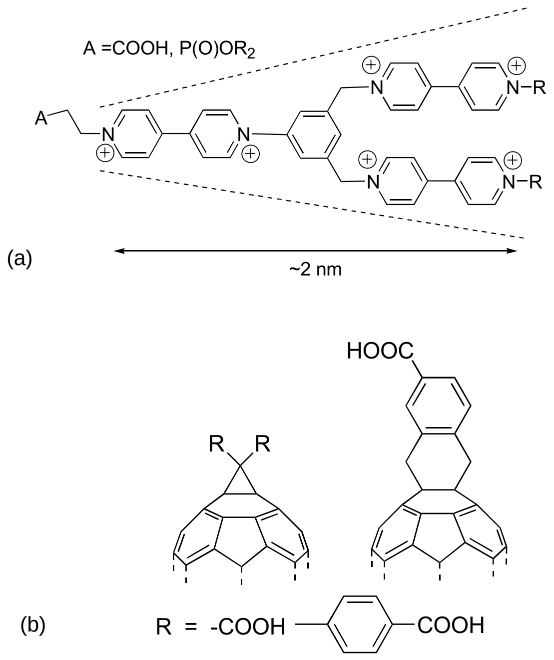
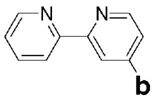
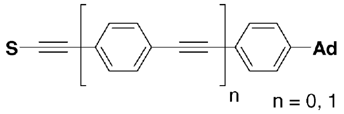
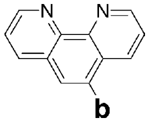
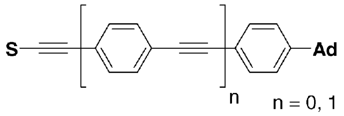
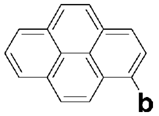
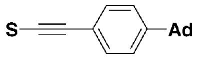
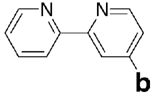
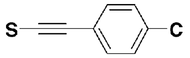
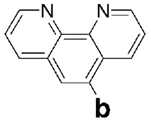
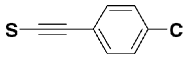
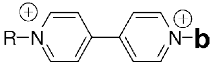
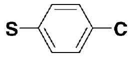
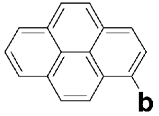
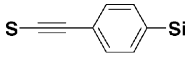


Fig. 12. Examples of other organic linkers. (a) Wedge-shaped viologen derivatives. (b) Fullerenes with anchoring groups.

Table 4
Tripodal linkers (for the structures, see Fig. 9)

Chromophore or ligand for metal complexes (**S**)	Entry	Bridge (**b**)	Anchoring group (**A**)	MO$_n$	References
From Ad-Tripods					
	1		COOR, R = Me, H	TiO_2, ZrO_2	[55a,68,69]
	2		COOR, R = Me, H	TiO_2, ZrO_2	[38,55a,68,69]
	3		COOR,	TiO_2, ZrO_2	[70]
From C-Tripods (n = 1)					
	4		COOR, R = Me, Et, H	TiO_2, ZrO_2	[38,55a,69]
	5		COOR, R = Me, Et, H	TiO_2, ZrO_2	[38,55a,69]
Porphyrins	6		PO_3H	TiO_2	[72]
From C-Tripods (n = 2)					
	7		PO_3Et_2	TiO_2	[71]
From Si-Tripods					
	8		COOR, R = Me, H	TiO_2, ZrO_2	[70]

groups (not shown) was prepared in an attempt to “wrap” the nanoparticle (Table 4).

Fullerene has attractive properties as a linker as well as a redox active compound because it is symmetrical, rigid, can be derivatized with good regioselectivity, it is a good electron acceptor and its photophysical and electrochemical properties are well characterized. Hence, the interest in taking advantage of the properties of C_{60} for semiconductor sensitization. Polymer/fullerene blends have been used as the active layer in photovoltaic cells [74]. Papageorgiou and coworkers have anchored fullerenes as a monolayer on the surface of nanocrystalline mesoporous ZrO_2 films through carboxylate anchoring groups, Fig. 12b [75]. The ZrO_2-bound fullerenes, when cast on ITO glass, exhibited reversible currents 200 times higher than those observed for the same fullerenes directly deposited on the conducting glass. In this case, the C_{60} unit is the linker as well as the electron acceptor, and participates in an electron hopping/percolating mechanism. Lateral charge transfer was observed over the entire thickness of the adsorbed fullerene layer. Effectively, the fullerene monolayer behaves as a conducting coating deposited on the nanoparticle. The authors have envisaged several possible applications that could take advantage of this property, including redox reactions of bound biomolecules.

3. Conclusions

Many future devices will consist of electrochemically active or photoactive molecules (sensitizers) interfaced with semiconductor nanoparticles. In order to be able to build such complex systems in a rational and predictable manner and to understand the interfacial electronic processes that are responsible for the devices functioning, it is necessary to find ways to control the position of the molecule on the surface, to tune the interfacial electronic processes and to control the aggregation phenomena. For this reason, rigid linkers of varying complexity, with large footprints and multiple anchoring groups are rapidly replacing simple alkyl chains. Recent studies have demonstrated that rigid linkers that have the shape of rods and tripods are able to fix the position of the sensitizers on the surface, that are useful models to investigate interfacial electronic processes and that can tune the properties of the sensitizer. The increasing interest in rigid linkers and more elaborate dyes demonstrates the significant role of molecular design in the field of photovoltaics.

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