Ferrocenylethynyl - A Versatile Platform for New Molecules to Novel Materials

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ABSTRACT: Ferrocenylethynyl is a key starting material for the synthesis of fascinating new molecules and novel functional materials. It combines the robust and redox-active ferrocene moiety with the rigid-rod ethynyl unit. The ferrocene center provides chemically and electrochemically switchable material properties whereas the ethynyl backbone facilitates electron delocalization along the molecule, yielding materials with the potential for a wide range of applications from sensors to bio-organometallics and pharmaceuticals, from catalysts to nonlinear optical materials, and from fuel additives to chelating agents. However, lifetime performances and costs still need to be optimized to make ferrocenylethynyl-based materials commercially competitive. Efficient synthetic methods are already in place which could play a key role in the progress of these materials. This review discusses the main approaches adopted in the synthesis of ferrocenylethynyl-based molecules and materials. Representative examples of each method are reported, highlighting its significant achievements together with the open issues and challenges to be faced by future researchers in this area.

Keywords: Ferrocene; Ethynyls; Electrochemistry; Synthesis; Organometallic.

فيروسينايل إيثينيل ـ منصة متعددة لجزيئات جديدة في تحضير مواد مبتكرة

حقيق الله شاه وريا البلوشية ومحمد صلاح الدين خان

ملخص: يعتبر فيروسينايل إيثينايل المادة الأساسية في تحضير جزيئات جديدة مهمة ومواد وظيفية. هذه المادة تجمع بين الفيروسين الذي يتميز بقوته وصلابته وقدرته النشطة على التأكسد والأختزال والإيثينايل المسطح. الفيروسين يوفر خصائص المواد التشغيلية الكيميائية والكهروكيميائية بينما وجود الإيثاين كخلفية للمادة يضمن عدم تمركز فعال للإلكترونات على طول الجزيء والذي يولد مواد ذات احتمالية للإستخدام في مدى واسع من التطبيقات من المجسات إلى العضوية الفلزية الإحيائية والأدوية ومن العوامل الحفازة إلى المواد الضوئية غير الخطية ومن مضافات الوقود إلى العوامل الإرتباطية إلى آخره. ولكن وبالرغم من ذلك، فإن كفاءة العمر الزمني والتكاليف بحاجة للتحسين لجعل مواد الفيروسينايل إيثينايل منافسة تجارياً. وتلعب التطويرات في منهاجية التحضير الفعّال دوراً هاماً في تفعيل هذا النوع من المواد. هذا العرض يناقش أهم ما تم التوصل إليه في تحضير الجزيئات والمواد المكونة أساساً من الفيروسينايل ايثينايل، ويتم خلال عرض منهجيات التحضير المختلفة طرح بعض الأمثلة التوضيحية مع إلقاء الضوء على النتائج المهمة التي تم التوصل إليها والتحديات التي يجب مواجهتها في الأبحاث المستقبلية في هذا المجال.

مفتاح الكلمات: فيروسين، إيثينايل، كهروكيميائية، تحضيروعضوية معدنية.

FERROCENYLETHYNYL - A VERSATILE PLATFORM

Contents

1. Introduction

Even six decades after its discovery, ferrocene still remains a hot topic for new materials researchers. Ferrocene and ferrocene-based materials are versatile and have been successfully used in a variety of domains such as electrochemistry [1-4], sensors [5], nonlinear optics and luminescent systems [6,7], pharmaceuticals [8,9], automobiles [10,11], fine organic synthesis [12], materials chemistry [13-17], liquid crystals [18-20], paramagnetic and ferromagnetic systems [21,22] and bio-organometallic chemistry [23], etc. During its long journey ferrocene chemistry has witnessed the emergence of many structural motifs built around the ferrocene platform, suitably grafting ene, phenylene(ethylene) and ethynyl spacers between two ferrocenes or between a ferrocene and an organic/inorganic group.

Compounds having an ene-terminus in the arm(s) are building blocks for metathesis and polymerization reactions leading to organometallic oligo/polymers or metallophanes. On the other hand, examples of motifs having conjugated all π-arms are relatively rare and are viewed as promising candidates in building nano-architectures. It is now generally accepted that an unsaturated adjunct acts as a messenger to facilitate communication between the arm and the redox centre.

This leads to synergistic perturbation of the electronic, opto-electronic and electrochemical properties of the molecule. Not surprisingly, compounds belonging to such motifs find end applications in diverse areas ranging from metallo-mesogens through NLO-active organometallics to redox-switch receptors. The significant potential of this special class of ferrocenes is expected to witness further exploration on many fronts.

Togni *et al*. [24,25] and others have shown that chiral and achiral ferrocenyl phosphines can be used as ligands in organic synthesis and asymmetric catalysis for carbon–carbon, carbon–heteroatom coupling, carbonylation, hydroformylation, hydrogenation, olefin polymerization and cycloaddition [26,27]. Gallei *et al*. have shown that the oxidation state of the ferrocene can affect the wettability of surfaces modified with poly(vinylferrocene) or poly(2-(methacryloyloxy)ethyl ferrocenecarboxylate) [28]. Kadkin has reviewed mono- and di-substituted ferrocenes containing liquid crystals and shown that liquid crystalline ferrocene exhibits unique physical properties [29]. Undoubtedly, the design motif in ferrocene-based architectures plays the most important role in delivering the targeted property. Linearly substituted ferrocenes having substitution at one or both cyclopentadienyl (Cp) rings constitute a very large sub-group of ferrocene architectures. Very

broadly, these are of three types - olefinic, ethynyl and cumulenic as shown in **Chart 1**. In the past two decades different research groups have developed a range of these architectures with the sole aim of tuning their chemical, electrochemical, spectroscopic and opto-electronic properties. As a result, they have gained prominence as new generation molecular materials, π-conjugated multi-metallic systems and as redox-switchable receptors.

In this review, we have concentrated on ferrocenyl alkyne type molecules and materials and focused on this special class of ferrocenyl materials, with a view to developing a comparative assessment of recent advances in their synthesis and properties. We have also attempted to look closely into these systems under sub-categories representing types of spacers in the backbone chain and to highlight selected examples.

1.1 Synthetic flexibility: Tuning the properties of Ferrocenyl Materials

Ferrocene derivatives with linear, unsaturated side-arms show unique properties compared to their saturated analogues. Some of these properties include electrical conductivity, thermal stability, magnetic, electronic, redox, and non-linear optical behaviour. This can be attributed to the electronic interaction of both metal- and ligand-based orbitals of ferrocene platform with the orbitals of the π-conjugated substituents in the side chain. Not surprisingly, some of the properties are dramatically dependent on the nature and conjugation length of the substituents. In this section, we closely look into these properties with special emphasis on the electronic, redox and optical effects of ferrocenes with an ethynyl conjugation. In the ferrocenyl alkynes, the linear alkyne arm(s) may bear all carbon or hetero elements, heterocyclic rings, conjugated and non-conjugated spacers and may have an extended π-conjugation with another ferrocene nucleus. Four structural types represent the majority of ferrocenes with a linear open-arm motif depending on whether the ferrocene nucleus is mono- or di-substituted or whether the ferrocene acts as a pillar to form "molecular clefts" (see **Chart 2**). Within the linear open-end motifs, those in which the ferrocene unit is connected to an unsaturated alkyne side-arm, π-conjugated to the Cp ring are of significant interest. Herein we review recent advances in their synthesis and properties and attempt to look closely into these systems under sub-categories representing types of attachments in the side chain and to draw attention to selected examples in detail.
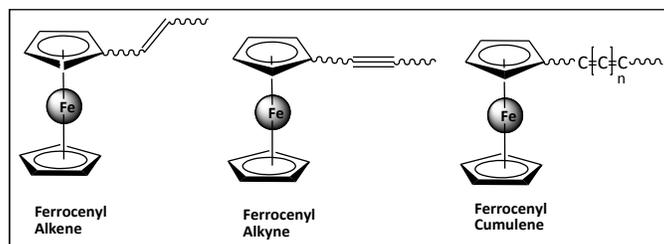

Chart 1. Linear structures of ferrocene.
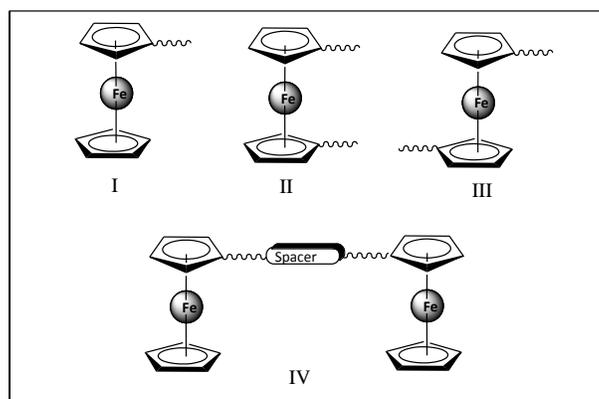
**Chart 2.** Types of ferrocenes with an unsaturated backbone.

2. Synthetic protocol for ferrocenylethynyl connected to conjugated organic spacers

Several methods for syntheses of ferrocenyls with an ethynyl backbone using the cross-coupling reactions, such as Sonogashira coupling, Negishi coupling, Stille coupling and Stephens-Castro coupling, have been reported in the literature (see **Scheme 1**). In this section, we examine the synthetic routes in detail.

Successive Sonogashira coupling of iodoferrocene with ethynyl substrates has been achieved in the presence of catalytic amounts of $PdCl_2((PPh_3)_2)/Cu(OAc)_2$ in $^iPr_2NH$ at 90 °C to give ferrocenylethynyl complex (**A**) in high yield [30]. Iodoferrocene has also been the starting material for the synthesis of many ferrocenylethynyl derivatives through various coupling pathways [31-33]. Stille coupling using 4-pyridyl(trimethylstannyl)ethyne and iodoferrocene has also been used to synthesize ferrocenylethynyl compound (**B**). Negishi coupling of the organozinc component with iodoferrocene has also been used for generation of extended ferrocenylethynyl (**C**) [34]. The Stephens-Castro coupling has been utilized by reacting iodoferrocene with the corresponding copper arylacetylide to synthesize arylferrocenylethyne (**A**) in 26–50% yield in refluxing DMF rather than the usual pyridine as solvent. It is noteworthy that refluxing equimolar amounts of iodoferrocene and cuprous phenylethynyl in pyridine for 8 h under N_2 provides the same ferrocenylphenylethyne (**A**) in 84% yield. In an analogous manner, coupling of iodoferrocene and cuprous ferrocenylethynyl produces the bis-(ferrocenylethynyl) (Fc-C≡C-Fc) in 85% yield.

2.1 Type I Ferrocene Materials

Among the methods described, Sonogashira coupling has been the most extensively used due to its good yield and better quality of end product [35]. Furthermore, most of the terminal ethynyl compounds are not stable in air and at ambient temperature. Ethynylferrocene is stable at room temperature, easy to handle and gives higher yield compared to the iodoferrocene starting material. Hence, it is a good choice as the key starting material for coupling reactions with the dihalo-aromatic and hetero-aromatic spacers to obtain the desired cross-coupled products. Often this reaction is accompanied by a minor by-product arising from the homocoupling of the ethynyl units, which can be avoided by maintaining a rigorous inert atmosphere. The (1:1) Sonogashira coupling of ethynylferrocene with mono-halo aromatics such as benzene, naphthalene, anthracene, etc., or mono-halo hetero-aromatics such as thiophene, pyridine, bipyridine, etc., or with mono-halo mixed hetero-aromatic ligands has given rise to novel compounds which have direct applications or which act as precursors for further new materials developments.
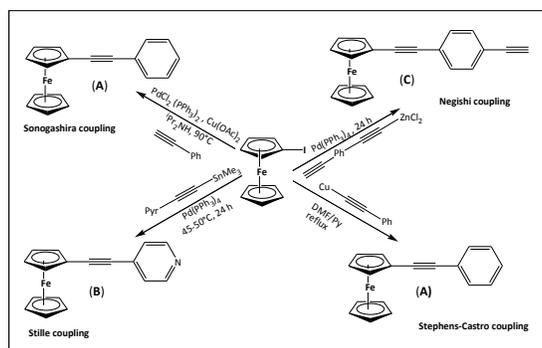
Scheme 1. Synthetic protocol for ferrocenylethynyl connected to conjugated organic spacers.

General representation of ethynylferrocenes capped with aryl and various substituted aryls (R) placed in conjugation with the ethynyl unit is shown in **Chart 3** [36]. The use of a wide range of 'R' shows that the reaction tolerates both electron-withdrawing as well as electron-donating spacers providing functional molecules and new materials [37]. For example, the compound prepared by the coupling of ethynylferrocene with 4-bromopyridine serves as a ligand with terminal pyridine as the coordinating site (**5,6**) [38]. A similar coordination site is also provided by dangling ligands like $4-BrC_6H_4C≡N$. The reaction leads to compound **7** in 84% yield [39]. This compound with an additional C≡N ligating site serves as the basis for the preparation

of oligonuclear ferrocene-based transition metal complexes [34,40]. By coupling ethynylferrocene with the appropriate mono-bromooligothiophene, substituted thiophene and fused thiophene unit, a new series of type I ferrocenyl derivatives has been synthesized (**8-12**) [41].

Compound **13** is a much more extended phenylethynyl congener linked to a metallic end-cap *via* a fluoren-9-one spacer [42]. Extended one-dimensional conjugated compounds (**14-16**) have also been synthesized by incorporating oligothiophene spacers on the ethynyl skeleton (**Chart 4**).
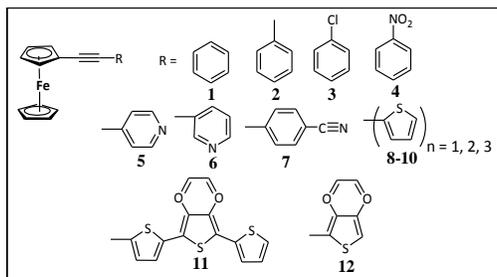

Chart 3. General chemical structures of some mono-(ferrocenylethynyl) derivatives.
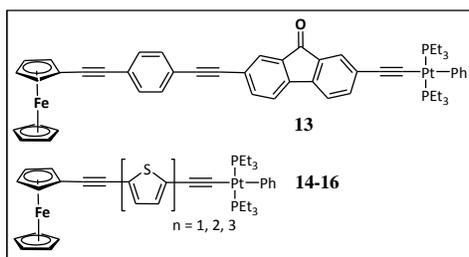

Chart 4. General chemical structures of one-dimensional mono-(ferrocenylethynyl)compounds with extended conjugation.
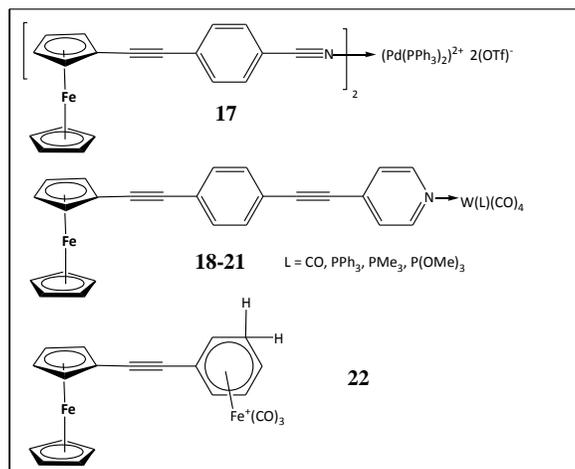
Chart 5. General chemical structures of mono-(ferrocenylethynyl) compounds.

Interestingly, placing a benzonitrile and pyridine group on the ethynyl skeleton has provided an added opportunity for further coordination to a metal complex precursor such as a Pd(PPh$_3$)$_2$ unit (**17**), giving rise to the trimetallic species and subsequent metal coordination to tungsten providing mixed-valence bimetallic fragments (**18-21**), that are potential candidates for molecular wires (**Chart 5**). Indeed, an insight into the

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delocalization along the conjugated backbone can be obtained from the analysis of their strong ligand to metal charge-transfer bands [34,40]. Ferrocenylethynyls capped with electron-accepting groups result in nonlinear optical properties. Compound **22** is an example having a tricarbonyl(cyclohexadienyl) iron(1+) unit acting as the electron accepting cap [43]. The interesting aspect of the molecule is that, it not only shows a high hyperpolarisability (γ) value of 100 x 10^{-30} esu (in comparison to $\gamma = 16.9$ x 10^{-30} esu for 4-nitroaniline), but also has a chiral electron accepting organometallic end-group. Thus, type I ferrocenylethynyls capped with aromatic, hetero-aromatic and metallic substituents are synthesized with the aim of exploiting optical, opto-electronic and other material properties.

2.2 Type II Ferrocene Materials

The second type of motif consists of two *cis*-disubstituted ferrocene units interlinked by extended ethynyl bonds. Examples of this type of ferrocenes are rare. In the late 60s, Hedberg and co-workers reported the synthesis of biferrocenylene (without the ethynyl bridge) [44], they were followed by Rosenblum and co-workers who reported the first member of this class of ferrocenes having bridging ethynyl groups [2.2]ferrocenophane-1,13-diyne (**see Chart 6**) [45].
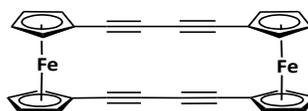
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Chart 6. Chemical structure of bi(ferrocenylethynyl) compound.

This was achieved by coupling of the cuprous salt of 1-ethynyl-1′-iodoferrocene. Later, Livanda and coworkers investigated this compound for its electrochemical properties and presented a comparison with the biferrocenylene [46]. The monocation of [2.2]ferrocenophane-1,13-diyne had a near-infrared band (λ 1760 nm, ϵ 2100) at lower energy and higher intensity than the corresponding biferrocenylene monocation [47]. The electrochemical and spectral results suggest that [2.2]ferrocenophane-1,13-diyne is a delocalized analogue of the biferrocenylene cation.

2.3 Type III Ferrocene Materials

The third type of motif consists of two *trans*-disubstituted ferrocene units linked by extended ethynyl units to form oligomers and polymers. Ingham *et al.* were the first to synthesize monomeric, dimeric and polymeric ferrocenylethynyls incorporating the phenylene spacer by reacting 1,1′-diiodoferrocene with mono- and bis-alkynyltrimethylstannanes [48].

They also reported a crystal structure of the bis(phenylethynylferrocene) which showed a *cis*-conformation. Yamamoto and co-workers [7] were one of the earlier research groups to report the synthesis of a series of ferrocenylethynyl polymers (**24-28**) incorporating carbocyclic and heterocyclic spacers using Sonogashira synthesis. They also reported a model compound (**29**) for comparison which showed *cis*-conformation similar to earlier reports (see **Chart 7**).
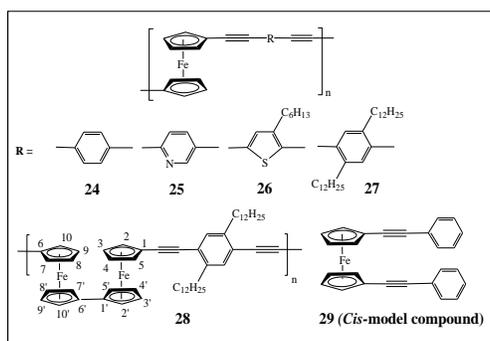

Chart 7. General chemical structures of ferrocenylethynyl polymers.

Electrochemical investigation of these materials showed broadening in the cylic voltammetry peaks. They compared the CV peak broadening of the poly(ferrocenylethynyl)s with that of a diphenylethynylferrocene model compound and further compared both of these with the CV peak of parent ferrocene. They found that the parent ferrocene peak compares well with that of the diphenylethynylferrocene model compound, which eliminated the involvement of the diethynyl bridging unit in the broadening of the CV peaks. Plenio *et al*. conducted a more systematic study by synthesizing a series of ferrocenylethynyl oligomers and performing a systematic evaluation of the cyclic voltammograms and also complementing the results by differential pulse voltammograms [49]. Both groups proposed that the broadening in the CV could be due to the presence of closely spaced redox processes of the adjacent ferrocene units in the polymer.

2.3.1 Electrical conductivity

Designing and preparing molecular wires with good charge transport capacity is of crucial importance to the development of molecular electronics. When ferrocene is incorporated in the organic chain it enhances the charge mobility along the chain. A recent report demonstrates how the conductivity of an oligo(*p*-phenylene ethynylene) chain (**30-36**) increases (**Figure 1**) by incorporating ferrocene into molecular backbones (**37-40**). Lu *et al*. [50] have successfully enhanced the molecular conductance of oligo(*p*-phenylene ethynylene)s (**30-36**) in both tunnelling and hopping conduction regimes. Specifically, they found that the increased degree of molecular conductance in the hopping regime is much more than that in the tunnelling regime [50]. In **Figure 1** a plot of ln R (R = resistance) *vs*. molecular length shows that molecules of the same length containing ferrocene i.e. (**37, 38, 39** and **40**) in the backbone have lower resistance which implies they have higher conductance compared to the purely organic oligo(*p*-phenylene ethynylene)s (**30, 32, 34** and **36**) respectively.

2.3.2 Electronic properties

The electronic structure of ferrocene includes three highest filled levels resulting from d_{xy}, $d_{x2−y2}$ (e_{2g}) and d_z^2 (a_{1g}) orbitals, which are essentially metal-based, while the next highest orbitals (e_{1u}) are principally ligand-based. The molecular orbitals resulting from the d_{xz} and d_{yz} bonding interactions (e_{1g}) are occupied, while the antibonding counterpart (e^*_{1g}) remains vacant. The molecular orbital energy level diagram of ferrocene and those with maximum d-character (highlighted in the box) are shown in **Figure 2** [51].

Generally, two prominent bands are observed for ferrocenyl compounds in the visible region. In agreement with previous experimental work and theoretical treatment, the higher energy band (300–390 nm) is assigned to a π–π* intra-ligand transition, and the lower energy band (400–500 nm) is assigned to a metal to ligand charge-transfer band (MLCT). In addition, another very weak band at higher wavelength (about 500 nm), assigned as d–d transition, is sometimes discernible as a shoulder on the MLCT band [52]. Attaching a conjugated system to ferrocene causes significant perturbation of the ligand-based (e_{1u}) orbitals. With increasing conjugation length, the energy of the π* orbital is lowered resulting in a red shift of the π–π* transition [53]. An increase in wavelength with degree of conjugation is also observed for the ferrocenylethynyl derivatives having fluorenone spacers. It is also clear that the increase in the number of ethynyl units from n = 1 to 2 leads to further red shift in the absorption maxima, consistent with the more extended π-conjugation. For example, there is a linear relationship reported between the λ_{max} for d-d transition and 1/n (n = number of ferrocenylethynyl units) for monomers and oligo-ynes with a limiting value of 472 nm for 1/n = 1/∞ (**Figure 3**).

These effects have been found to be linear in ferrocenylethynyl poly-ynes and oligo-ynes. In addition, the extinction coefficient is reported to increase with 'n'. It is thus evident that the ferrocene d-d transition is coupled to the conjugated main chain [49]. The spectra and extinction coefficients of the ferrocenylethynyl oligo-ynes in CH_3CN and CH_2Cl_2 show only a weak solvatochromic effect between the two solvents. Since solvatochromic behaviour reflects the polarizability of a chromophore, studying the electronic spectra provides an important means to measure the magnitude of nonlinear properties in a donor-acceptor bridged molecule [49].
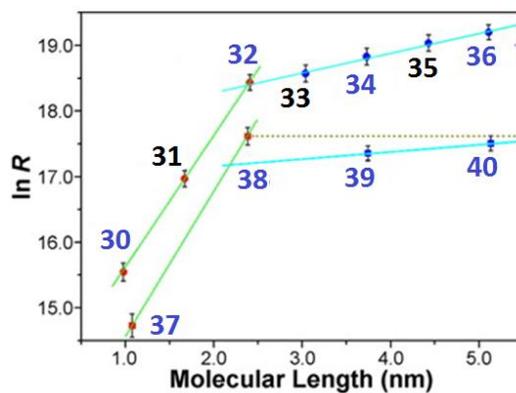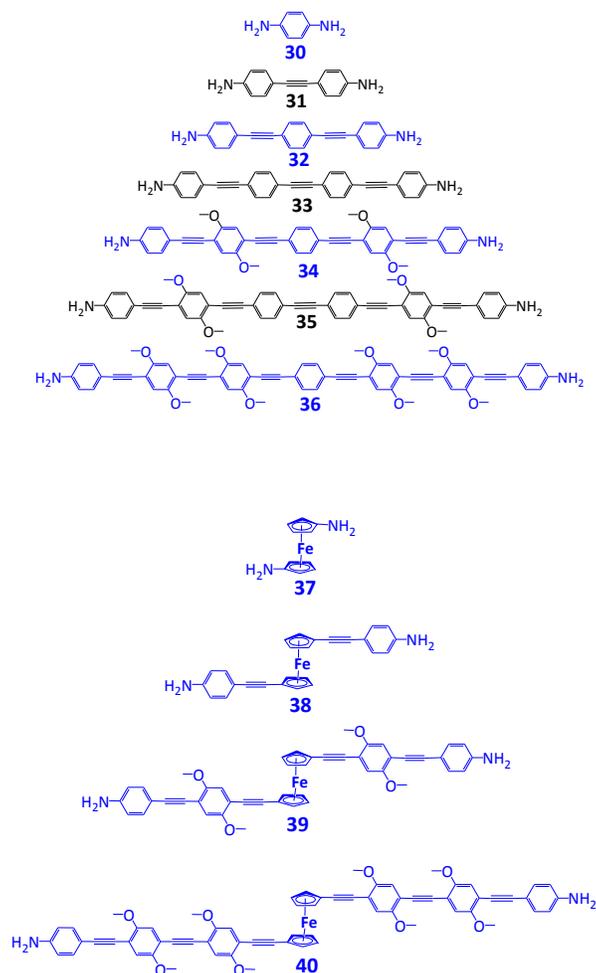
Figure 1. Chemical structures of oligo(*p*-phenylene ethynylene) chains (**30-36**) without and with ferrocene (**37-40**) and plot of ln R *vs.* molecular length (bottom). Adapted with permission from ref [50]. Copyright (**2012**) American Chemical Society.
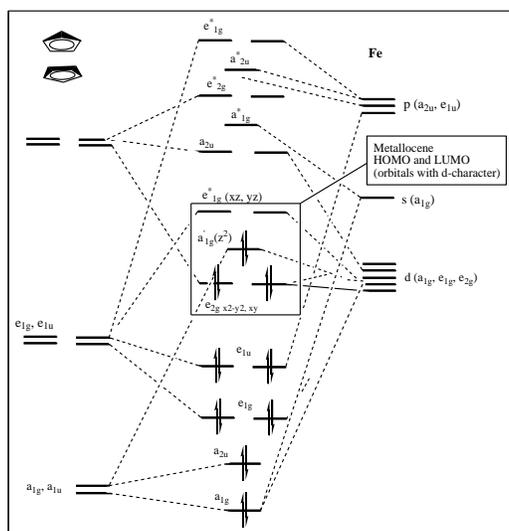
Figure 2. Molecular orbital energy levels in ferrocene. Adapted with permission from ref [51].
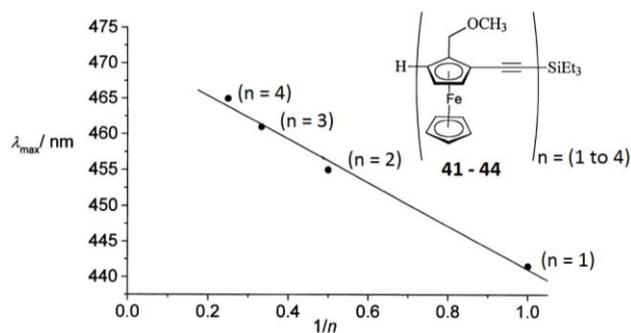

Figure 3. Plot of variation of λ_{max} with $1/n$ (λ_{max} d-d transition, n = number of ferrocene). Adapted with permission from ref [49]. Copyright (**2000**) WILEY-VCH Verlag GmbH, Weinheim.
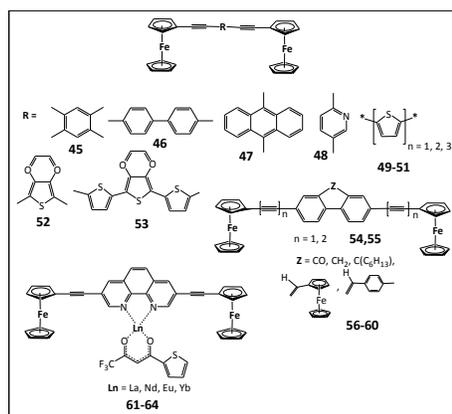

Chart 8. Selected bis(ferrocenylethynyl) compounds.

2.4 Type IV Ferrocene Materials

The fourth type of motif consists of two ferrocene units linked by ethynyl fragments and organic/inorganic spacers. By tuning the size and shape of the spacers, elegant molecular architectures with possible electronic communication between the metal centres along the conjugated backbone have been achieved. The Sonogashira coupling has also been extended to the bis(ferrocenylethynyls) by reacting ethynylferrocene with dihaloaryl precursors in the presence of $PdCl_2(PPh_3)_2$ and CuI catalysts in refluxing ^{i}Pr$_2$NH. Similar to the mono(ferrocenylethynyl) compounds, a variety of bis(ferrocenylethynyl) compounds have been prepared by incorporating aromatic, hetero-aromatic, mixed hetero-aromatic and metal bridging ligands. A few representative examples are shown in **Chart 10**.

A few examples of ferrocenyl end-capped ethynyl complexes incorporating a wide range of aromatic and hetero-aromatic spacers (R) are presented in **Chart 8** [44,41,53,54]. The electron donating or electron withdrawing properties of the conjugated spacer groups have been used to tune the redox properties of the ferrocenylethynyl dyads (**45-51**) [35,54]. Zhu *et al.* demonstrated that the potential difference (ΔE) between the two redox waves of the bis*(*ferrocenylethynyl) can be varied from 0.38 to 1.12 V, depending on the length and substitution of the oligothiophene group (**49-53**) [41]. Along this line, Wong *et al.*[53] designed a series of ferrocenyl end-capped derivatives (**54-55**) by varying the number of ethynyl units and the nature of the fluorene spacer in order to study the combined effect of the nature of spacer and the number of ethynyl units [53]. Electrochemical studies reveal that the half-wave potential of the terminal ferrocene becomes more anodic upon increasing the number of ethynyl units. Secondly, on changing the 9-substituent of the central fluorene ring from electron-rich alkyl (**57**) or ferrocenyl group (**59-60**) to an electron-deficient oxo group (**56**), the half-wave potential of the terminal ferrocene can be made more anodic. Yuan *et al*. have designed a series of bis(ferrocenylethynyl) complexes incorporating 1,10-phenanthroline spacer [55]. These bidentate ligands were used to synthesise a series of rare-earth β-diketonate complexes **61-64**. The presence of ferrocene in these complexes has been reported to shift the ligand absorption band to longer wavelengths, which in turn facilitates the excitation of these complexes by ultraviolet radiation and also by visible light.

2.4.1 Effect of spacer groups

Shah *et al*. recently reported a new series of bis(ferrocenylethynyl) complexes incorporating novel heterocyclic spacers [1]. They also synthesized one mono(ferrocenylethynyl) compound for comparison with the bis(ferrocenylethynyl)s (see **Chart 9**). The objective was to create donor-acceptor type structural motifs to enhance the communication between the two ferrocene termini. Broadened CV peak potentials for complexes **66-70** were observed without significant splitting of the mid-point potential. This was attributed to considerably longer Fe-Fe distance of around ~14 Å in complexes **66-70**, as established by X-ray crystallographic studies. Plenio and others have attributed similar broadening of the CV peak to the presence of closely spaced redox processes in those ferrocenylethynyl poly-ynes and oligo-ynes reported previously [49,56-58]. The CV features were reproduced by digital simulation which confirmed that the broadening in the CV peaks can be reconciled with the presence of two individual, closely spaced, one-electron processes (see **Figure 4**). The $\Delta E_{1/2}$ values suggest that they belong to Class II according to the Robin and Day classification scheme, with modest coupling [59].
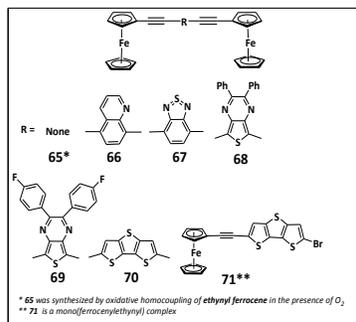

Chart 9. Chemical structures of bis(ferrocenylethynyl) complexes (**65-70**) and a mono(ferrocenylethynyl) complex (**71**).
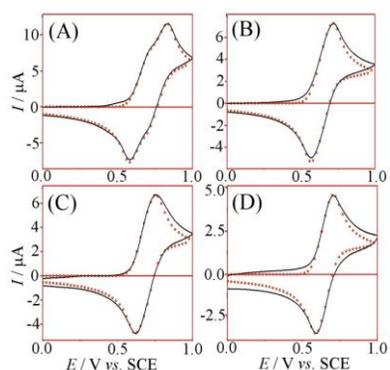
Figure 4. Selected simulation curves (red circles) matched with cyclic voltammograms (black line) for bis(ferrocenylethynyl) complexes **65**(A), **66**(B), **68**(C) & **70**(D). Reprinted with permission from ref [1]. Copyright (**2013**) American Chemical Society.

Recent reports suggest that electron withdrawing spacers play a positive role in improving the communication between the terminal ferrocene units [60-62]. Solntsev and co-workers demonstrated significant electronic communication in bis(ferrocenyl) complexes separated by electron withdrawing spacers having Fe-Fe distance <8Å [60]. Similar trends were seen in complex **67**. Despite a Fe-Fe distance of 13.494 Å, it showed $\Delta E_{1/2}$ 110 mV, which was not too dissimilar compared to values for *para*-diferrocenylbenzene [63]. The electron withdrawing nature of the spacer influences the net conjugation effect over-riding the Fe-Fe distance separation in this particular comparison. Another example demonstrating the effect of the spacer group is the bimetallic complexes reported by Mercs *et al.,* where the bis(NHC) spacer exhibited weaker interactions ($\Delta E_{1/2}$ = 42−80 mV) despite having direct metal-NHC connections and Fe-Fe distances of less than 11 Å [56]. Complexes **66-70** with Fe-Fe distance of ~14 Å and $\Delta E_{1/2}$ values of 50 to 110 mV represent long-range intra-molecular electronic communication [64,65].

The formation of the monocationic species was investigated by spectro-electrochemical methods (**Figure 5**). The changes in the spectrum in response to the applied potential confirmed the formation of an IVCT band as a result of mono-oxidation. The spectro-electrochemical experiments showed that upon oxidation of reported complex **65** to **65**[+], the intensity of the low energy MLCT bands decreases, while the intensity of the higher energy, predominantly π - π* band, increases. The NIR band was assigned as an IVCT transition as this band disappears on further oxidation by increasing the potential [64]. Similar observations were found for complexes **66-70**. The IVCT nature was further confirmed by comparing the bis(ferrocenylethynyl) complexes with the mono(ferrocenylethynyl) complex, both containing the dithienothiophene spacer. The mono(ferrocenylethynyl) complex **71** showed no band in the NIR region; instead it showed a band at 760 nm which was assigned as a LMCT band and has been previously reported for mono(ferrocenylethynyls).

Complexes **65** and **67** were studied computationally to get a better insight into the intra-molecular interaction processes (see **Figure 6**). For **65** the HOMO shows extensive delocalization across the whole molecule, with contributions of 26 (Fe), 11 (C_5H_4) and 23% (C≡C-C≡C) from the contributing fragments. Similarly, the HOMO for **67**, though less symmetrical than for **65**, has contributions of 33, 20 (Fe, Fe), 11, 8 (C_5H_4, C_5H_4), 7, 7 (C≡C, C≡C) and 14% (C_6NSN).

2.4.2 Effect of chain length

Electrochemistry has been extensively used to study the property sequence that occurs on changing the length and nature of the conjugated substituents attached to the ferrocene platform. Chain lengthening of the π-conjugated system results in a non-linear decrease of the redox potentials due to charge delocalization and stabilization of the ferrocenium formed. Good dependence of chain lengthening and redox potential is observed in the ferrocene dimers with ethynyl bridges. Due to the two redox centres, these complexes are expected to show two redox potentials. The peak separation denoted by $\Delta E_{1/2}$ indicates the extent of

internuclear electron transfer. Dependence of electron transfer with chain length is clearly established in the bis(ferrocenylethynyls) such as $Fc_2(C\equiv C)_n$ (n = 0, 1, 2, 3,) [46,65,66]. Another notable feature is the dependence of the Fc/Fc^+ redox potential on the chemical nature of the conjugated spacer group in the ferrocenyl derivatives. Electron withdrawing fragments attached to the terminus of the conjugated spacer stabilize the neutral Fc over the cationic Fc^+, and result in an anodic shift of the redox-wave compared to that of the free ferrocene.
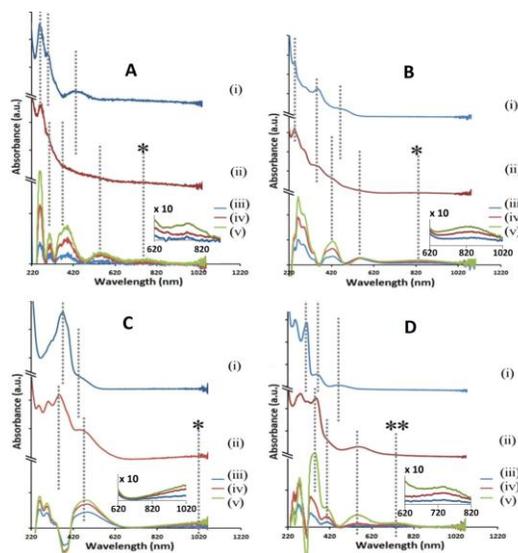

Figure 5. UV-vis spectra of complexes **65**(A), **66**(B), **70**(C) & **71**(D). (i) data for the neutral spectra, (ii) the mono-cation, and difference spectra (iii-v) are shown. Adapted with permission from ref [1]. Copyright (**2013**) American Chemical Society.

Some good examples are given by Maragani *et al*. who have synthesized a series of monofunctionalized ferrocenyl ethynyls and investigated the donor-acceptor interaction between the ferrocene and the ligands [67]. In the bis(ferrocenylethynyls), the nature of the spacer group has been very well utilized to tune the redox properties and the intra-molecular electronic communication of the complexes [35,53]. Wong *et al*. have incorporated electron-rich and electron-deficient groups in the bis(ferrocenylethynyl) complexes and presented a systematic study of the redox behaviour of the ferrocenes. The study reveals that the redox potential can be made anodic with the use of electron-deficient spacers in the bis(ferrocenylethnyls) and vice versa. In the same report, they also varied the $(C\equiv C)_n$ unit from 1 to 2 and found that the increase in the ethynyl unit also increased the redox potential in the complexes [53].
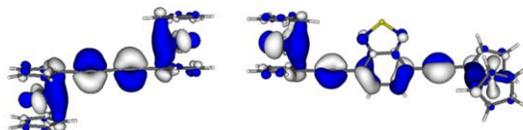
Figure 6. HOMO of complexes **65** (left) and **67** (right). Reprinted with permission from ref [1]. Copyright (**2013**) American Chemical Society.

2.4.3 Effect of electrolyte

There are few examples of higher number of ferrocenes connected through a bridging organic spacer. Compound **72** reported by Fink *et al*. having three ferrocene termini connected by the triethynylbenzene core is noteworthy as it may be viewed as a potential precursor for the production of metal-aromatic poly-yne

networks [69]. Diallo *et al.* have reported examples of six ferrocenes connected to a hexaethynylbenzene core [69]. They demonstrated that redox chemistry of such molecules is highly sensitive to an ion-paring dependant electrostatic effect. They used substituted and un-substituted ferrocene and presented a fine work of electrochemistry demonstrating the effect of a supporting electrolyte on the redox process of these complexes (see **Chart 10**).

    Figure 7 shows the CV of the tri-ferrocenylethynyl benzene and hexa-ferrocenylethynyl benzene. The top figures show the CV from the traditional electrolyte *i.e.* tetrabutyl ammonium hexafluorophosphate, while the bottom CVs resulted on changing the electrolyte to tetrabutyl ammonium tetra aryl borate. This change in the electrolyte resulted in separation of the ferricenium signals as shown in the bottom figures. Similarly, when one of the hydrogens on the Cp in the hexa-ferrocenylethynyl benzene was substituted with methyl groups, all the six CV signals could be separated.
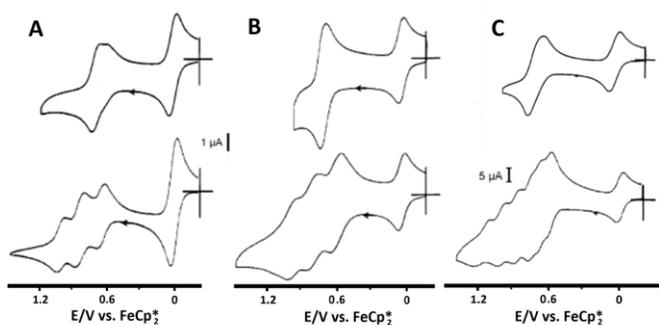
Figure 7. CVs of complexes **72(A)**, **73(B)** and **75(C)** under [*n*-Bu$_4$N]PF$_6$ (top) and [*n*-Bu$_4$N]BAr$_4$ (bottom) electrolyte. Reprinted with permission from ref [69].
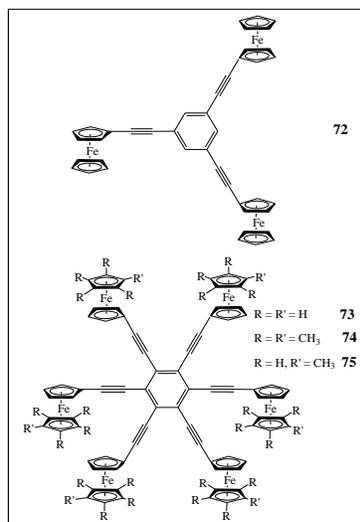

Chart 10. Chemical structures of tri- (**72**) and hexa-ferrocenylethynyl complexes (**73-75**) investigated by Diallo *et al.* [69].

3. Ferrocenylethynyls connected through a metal bridge

3.1 Ferrocene termini linked to metal bridge by covalent bond

Since the last decade intense efforts have been made to generate ferrocenylethynyls containing different metal bridging groups [70-73], or metal-containing fragments [74], in the study of electronic communication between the redox-active termini through organic [63,75] or metal-containing fragments [74].
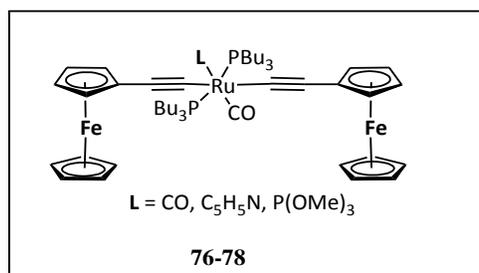

Chart 11. General chemical structure of ferrocenylethynyls connected through ruthenium metal units.

The compounds shown in **Chart 11** are a few good examples of ferrocenylethynyls containing different metal bridging groups [74]. These are synthesized by a multi-step process and the ancillary ligand '**L**' on the central metal is varied to tune the interaction between the ferrocene termini. Interestingly, it was found that the Fe-Fe interaction is enhanced when an electron donating ligand is used, and reduced when the ligand is electron withdrawing. The dependence of the electronic communication between the two ferrocene units on the ancillary ligand at the central ruthenium metal lying in conjugation to the extended ethynyl chain demonstrates the potential of the metal bridging units.

3.2 Tuning the properties by metal bridging

Besides the study of electronic communication between the redox active termini through organic spacers [63,75], efforts have also been made to generate ferrocenylethynyls containing different metal bridging groups during the last decade. In these studies, ferrocenyl pendant groups are commonly used as redox centres, and ethynylferrocene commonly serves as the key starting material. Placing equivalent redox-active groups as end-caps in molecular arrays is often used to evaluate whether intra-molecular electronic communication occurs through metal-containing fragments and clusters. They have been attached to mono-[70,72,76,77] or dinuclear [78,79], organometallic and coordination compounds. However, examples of metal clusters capped by equivalent ferrocenyl groups are rare.

3.2.1 Electro-luminescence property

The example below from Albinati *et al*. [80] shows a bis(ferrocenylethynyl) complex (**79**) where the Fc units are connected *via* a $Pt_6(\mu\text{-PtBu}_2)_4(CO)_4$ metal cluster (**Figure 8**, top). No significant electronic communication was observed between the two terminal Fc units as shown by the unsplit redox wave at 0.3 V (**Figure 8**, bottom).

When investigated by spectro-electrochemistry, this compound, upon oxidation, gave an emission in the visible region. The emission band was carefully examined and found to be resulting from the metal cluster unit. This implies that the redox property of the ferrocenes in the molecule could be controlled by external application of visible light. It was suggested that the emission energy generated by the central metal cluster component could be utilized in three different ways as typified in **Figure 9**.

Type-D means that the metal cluster could be utilized as electron donor to the adjacent acceptor units, type-A represents the metal cluster as acceptor component which accepts electron from the adjacent units and A:D type means that the metal cluster is utilized in a way that can help the electron flow from the donor unit to the acceptor unit.
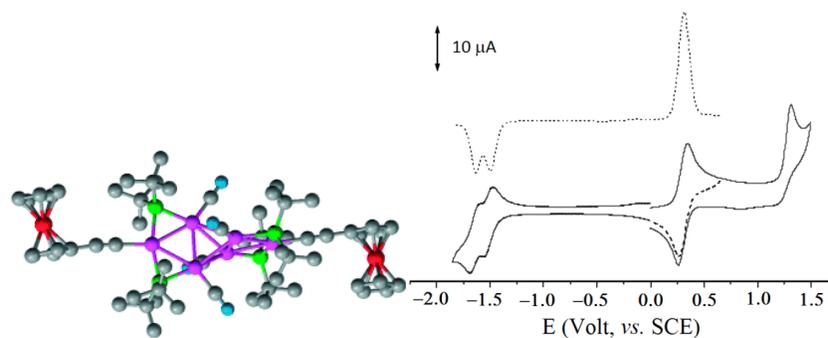
Figure 8. Crystal structure of $Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(C\equiv C\text{-}Fc)_2$ (**79**) (see structure: purple Pt, red Fe, green P, blue O; Fc = $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)]$) ($C_2Fc_2$) (left) and CV and DPV (right). Reprinted with permission from ref [80]. Copyright (**2005**), Wiley-VCH.
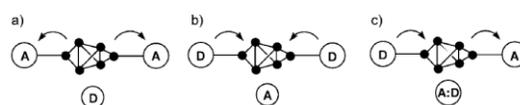

Figure 9. Schematics of charge flow in $Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(C\equiv C\text{-}Fc)_2$ complex. Reprinted with permission from ref [80]. Copyright (**2005**), Wiley-VCH.

3.2.2 Electronic communication

Another example of metal cluster assisted efficiency enhancement is given by Xu *et al.* (see **Figure 10**) [81]. They reported that insertion of a $Ru_2(DMBA)$ bridging unit into the 1,4-bis-(ferrocenyl)butadiyne $[(C_2Fc)_2]$ (**80**) dramatically enhances the electronic coupling between two Fc units in the $Ru_2(DMBA)_4(C_2Fc)_2$ complex (**81**).
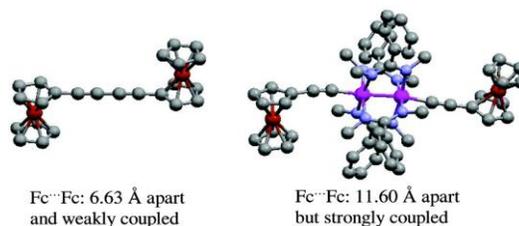
Figure 10. Crystal structure of C_4Fc_2 (**80**) left and $Ru_2(DMBA)_4(C_2Fc)_2$ complex (**81**) right. Reprinted with permission from ref [81]. Copyright (**2004**) American Chemical Society.

Although the distance between the two termini in $Ru_2(DMBA)_4(C_2Fc)_2$ is significantly larger (11.60 Å) than in the bis(ferrocenyl)-1,4-butadiyne (6.63 Å), the strong electronic coupling results from the metal cluster which can act as the bridge assisting the electron flow in one direction (type-A:D as explained above). The work was further extended to explore if the metal bridge can assist the coupling when the distance between the ferrocene termini is further increased by adding ethynyl units (**Figure 11**).
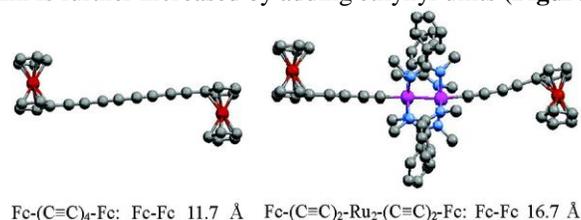
Figure 11. Crystal structure of C_8Fc_2 (**82**) and *trans*-$(FcC_4)Ru_2(Y\text{-}DMBA)_4(C_4Fc)$ complex (**83**); here Y-DMBA is N,N'-dimethylbenzamidinate. Reprinted with permission from ref [82]. Copyright (**2005**), American Chemical Society.
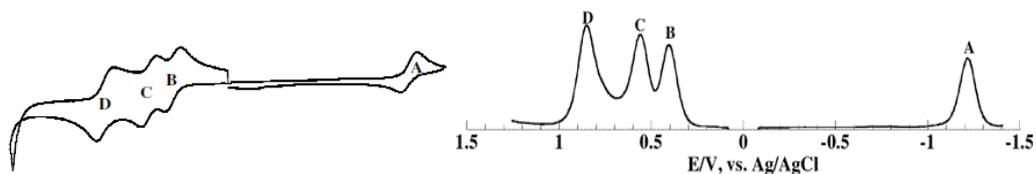
Figure 12. CV and DPV of $Ru_2(DMBA)_4(C_2Fc)_2$ complex. Reprinted with permission from ref [83]. Copyright (**2004**), American Chemical Society.

It was observed that the metal bridge allowed efficient coupling even on increasing the distance between the ferrocene units. The CV and DPV of $Ru_2(DMBA)_4(C_2Fc)_2$ (**Figure 12**) consists of one one-electron reduction at -1.22 V (**A**) attributed to the Ru_2 core, and three one-electron oxidations (**B**−**D**) between 0.4 and 1.0 V. One of the three oxidations is Ru_2-based because all $Ru_2(DMBA)_4(C_2R)_2$ compounds undergo one-electron oxidation in this region [83]. The DPV peaks were assigned after confirmation from the spectro-electrochemistry results which showed the clear increase and decrease in the peaks **C** and **D** upon sequential oxidation of the terminal ferrocenes. They also examined the spectral absorption band on oxidation which further supports that peaks **C** and **D** belong to the oxidation of ferrocenyl units.

3.2.3 Redox control

Ferrocene can work as an electron reservoir, and its metal-assisted assembly is highly intriguing in terms of molecular quantum devices, as demonstrated by Long *et al.* in a cobalt complex containing four ferrocenes shown in **Figure 13** [70,84].
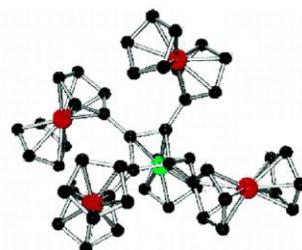
Figure 13. Crystal structure of $(\eta^5\text{-}C_5H_5)_2Fe)_4(\eta^4\text{-}C_4)Co(\eta^5\text{-}C_5H_5)$ complex (**84**). Reprinted with permission from ref [70]. Copyright (**2005**), American Chemical Society.
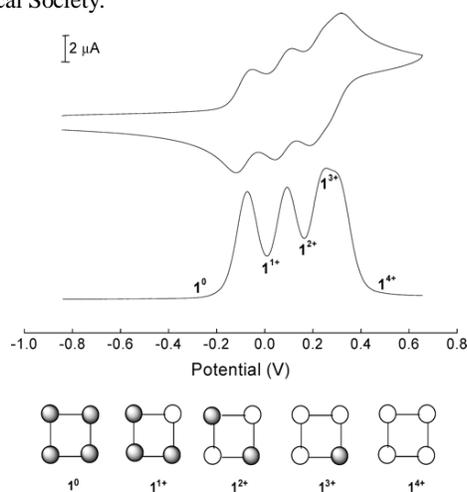
Figure 14. CV and DPV of $(\eta^5\text{-}C_5H_5)_2Fe)_4(\eta^4\text{-}C_4)Co(\eta^5\text{-}C_5H_5)$ complex (**84**). Reprinted with permission from ref [70]. Copyright (**2005**) American Chemical Society.

Complexes containing two ferrocenes communicating with each other are considered as building blocks of quantum cellular automata, where the ferrocenes can be sequentially oxidized and reduced to conduct the signals in single molecular electronic devices. Similarly, complexes with a higher number of ferrocenes are of special interest for logic gates like applications. Long *et al*. isolated the different oxidized forms of the complex shown below. In a 1:1 mixture of CH_3CN and CH_2Cl_2 the cyclic and square wave voltammetry gave good resolution with unambiguous evidence of three redox couples as can be seen in the voltammograms (see **Figure 14**).

In addition, the unresolved structure in the peak at the most positive potential in the square wave voltammetry suggests the presence of a fourth couple. The $E_{1/2}$ potentials for the $\mathbf{1^0/1^{1+}}$, $\mathbf{1^{1+}/1^{2+}}$, $\mathbf{1^{2+}/1^{3+}}$, and $\mathbf{1^{3+}/1^{4+}}$ couples are −0.085, 0.075, 0.225, and 0.283 V, respectively ($\Delta E_p = 0.08 \pm 0.02$ V), relative to the potential for the ferrocene/ferrocenium couple [70].

3.3 Ferrocene termini linked to a metal bridge by a coordination bond

The ferrocenylethynyls containing different metal bridging groups were produced by multi-step covalent synthesis methods. These types of syntheses are labour intensive and frequently suffer from low yield of the final product. Also the final products are quite often not stable under aerobic conditions. Coordination-driven synthesis emerged as a breakthrough to overcome many of these problems associated with purely covalent synthesis methods. Rationally designed self-assembled supramolecular structures that create self-organized, functional materials are of fundamental interest for application in catalysis [85], gas storage or gas/molecule separations [86], in nanotechnology [87,88], and in electronic materials [89,90]. Organic molecules can self-assemble into well-ordered structures, but often with limited conductance. Conductivity can be influenced and improved by using coordination complexes in which metal centers are incorporated into a molecular backbone. Such structures self-assembled on insulating surfaces have been reported for highly conducting nano-ribbons [89]. Solution based rational self-assembly is a promising approach for the formation of microstructures with desired shapes [91-93].

Scientists have coupled ferrocene to coordinating ligands like pyridine, benzonitrile, etc. and utilized these ferrocenyl derivatives to construct a wide range of metal complexes. The beneficial redox property of the ferrocene is successfully exploited in designing coordination complexes with supramolecular assemblies which would be impossible by conventional covalent synthesis. The use of ferrocene containing ligands imparts redox switching, mixed-valence and offers a host of other interesting properties to the coordination complexes.

In addition, incorporation of ferrocenyl or ferricenyl building blocks offer further material tuning opportunities and access to novel mixed-valence materials [94,95]. Ferrocenyl functionalized coordination complexes are of particular interest due to the robust and switchable chemical nature of the ferrocene. Ferrocene also exhibits attractive electrochemical features: fast electron-transfer rate, low oxidation potential, and two easily accessible stable redox states (neutral ferrocene and oxidized ferricenium). Ferrocene-modified surfaces have been demonstrated to efficiently communicate *via* a lateral electron hopping process[96,97] and were recently highlighted for applications in charge storage components and in semiconductor-based memory devices with the bound ferrocene center as the memory element [98].
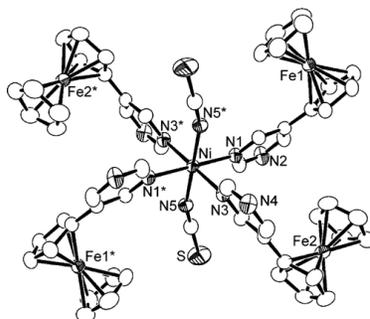

Figure 15. Crystal structure of tetra(ferrocenylpyrimidinyl)Ni(SCN)$_2$ complex (**85**). Reprinted with permission from ref [98]. Copyright (**2003**), American Chemical Society.

A good example of beneficial mono functionalization of ferrocene with a coordinating ligand and its use to obtain novel coordination complexes was given by Horikoshi *et al*. [99]. A simple ferrocenyl pyridine ligand when combined with transition metal salts, produce mixed-metal polynuclear complexes with structural diversity. Reaction of 5-ferrocenylpyrimidine with $M(SCN)_2$ (M = Ni, Co) produces the pinwheel-like 4:1 complexes (Ni complex (**85**) shown in **Figure 15**). The complexes are regarded as electro-active ferrocene clusters.

Some other strategies have also been proposed to obtain coordination complexes of varied size, shape and chemical combinations. The coordination of bifunctionalised ferrocene with a pyridinyl group to the metal "nodes" was utilized by Wei *et al*. [100]. The primary structure formed by coordination bonds in cooperation with weak non-covalent interactions, such as H-bonding and π stacking, organizes these primary structures into supramolecular architectures [101]. The self-assembly of small "building blocks" with transition metal ions generates cages, capsules, macrocycles, helices, networks, and other supramolecular architectures (**Figure 16**) for research in supramolecular chemistry, materials chemistry, and crystal engineering [102-104]. Careful design and synthesis of these novel architectures are essential for the creation of new functional materials with solvent inclusion or gas-adsorption characteristics or with special optical, electronic, magnetic, and catalytic properties [105,106].
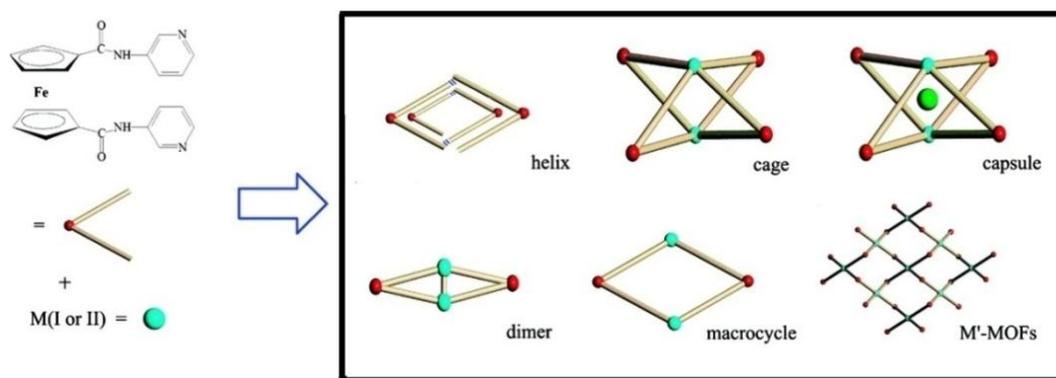

Figure 16. Chemical structure of bifunctionalised ferrocene with pyridinyl group (left) and their possible structure with metal (right). Reprinted with permission from ref [99]. Copyright (**2010**), American Chemical Society.

Copper(I) is well recognized for its ability to form multi-nuclear (cluster) species of various shapes and sizes, on reaction with a range of bridging and terminal ligands. In these clusters weak bonding interactions between the closed-shell metal centers are generally present [107-111]. A range of different architectures broadly categorized as **A** to **D** generating network and chain structures shown in **E** to **H** have been reported (see **Figure 17**). These clusters such as rhomboid $(CuX)_2$ dimers [111,113-115], cubane$(CuX)_4$ tetramers [114-116], infinite $(CuX)_\infty$ zigzag [117-120] or stair-step polymers [117,118] (X= halide) have been investigated by many research groups for their rich photo-physical properties. Structures with pyridine ligands in particular have been extensively studied for their extraordinary photoluminescence properties [121-130].
Several strategies for rational syntheses of complexes with four redox sites have been reported. These often require considerable synthetic effort to prepare, and can be plagued by low yields and largely amorphous final structures. When issues such as structural precision, synthetic ease and building-block versatility come into question, coordination-driven self-assembly provides a powerful alternative to the purely covalent synthesis of multifunctional molecules [125]. At the molecular level a symmetric mixed-valence complex is the building-block for the quantum-dot cellular automata [70]. Arrays with four redox sites are also considered more versatile for efficient cell designs in logic applications [85,126]. Functionalization of the Py-x to ferrocenylethynylpyridine in the $(CuX)_4(Py-x)_4$ series has allowed ready access to a series of tetraferrocenylethynylpyridinyl copper complexes (**86-88**) and, in the presence of triphenylphosphine co-ligand, gave di(ferrocenylethynylpyridinyl triphenylphosphine)copper square complexes (**89-91**) *via* coordination-driven self-assembly (see **Scheme 2**).
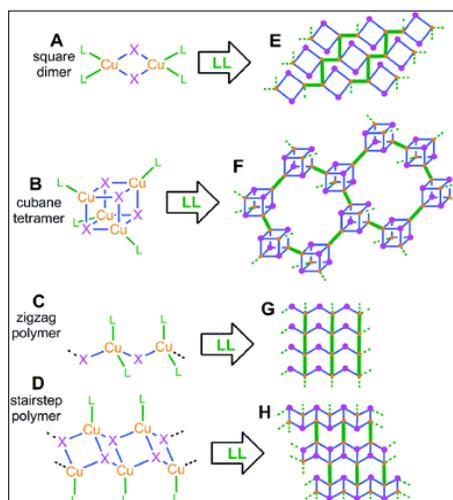
Figure 17. Different architectures obtained from Cu-halide in the presence of coordinating ligands. Reprinted with permission from ref [110]. Copyright (**2012**), The Royal Society of Chemistry.

The tetra(ferrocenylethynylpyridinyl) copper complexes undergo partial or full oxidation under mild electrochemical conditions and the electro-crystallized products show distinct morphologies such as dendritic for complex **86** while lettuce or flower like for complexes **87** and **88** (see **Figure 18**). For the electro-crystallized di(ferrocenylethynylpyridinyltriphenylphosphine) copper complexes (**89-91**), the SEM analysis confirmed the spontaneous formation of electro-crystallized full oxidation products with distinct morphology such as leaf-like for complexes **89** and **90**, and cabbage-like morphology for complex **91** (see **Figure 18**).
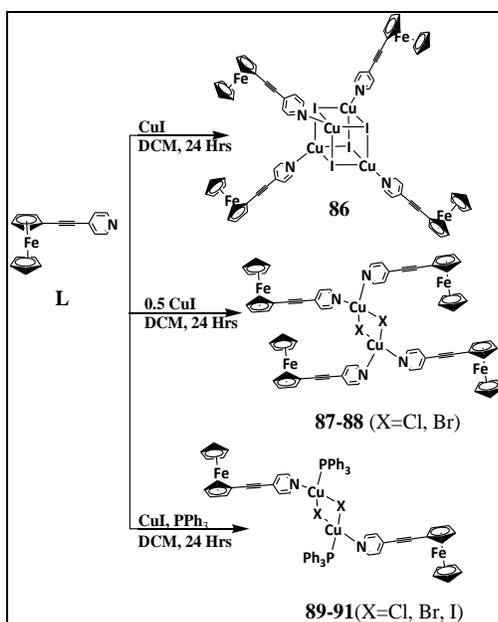
Scheme 2. Synthesis of tetra(ferrocenylethynylpyridinyl) copper halide complexes (**86-88**) and di(ferrocenylethynylpyridinyl triphenylphosphine) copper halide complexes (**89-91**).

Copper compounds are widely used as catalysts and electro-deposited Cu-based microstructures are of interest for applications in catalysis [129-132]. Furthermore, the shapes of the electro-deposited

microstructures have been shown to enhance the catalytic activity and selectivity of metallic catalysts [132]. Thus, the three types of distinct morphologies observed for the electro-crystallized products by changing the chemical composition (X = Cl⁻, Br⁻, I⁻) indicate the potential of the system for controlling the shape of the electro-deposited microstructures.

Recently, Noorduin *et al*. have demonstrated the potential of systematic change in the chemical composition during layer by layer growth of their crystal. They grew the crystals layer by layer to obtain novel microstructures as shown in **Figure 19**. Using this strategy they were able to generate a beautiful library of microstructures [133].

The electro-crystallized di(ferrocenylethynylpyridinyl triphenylphosphine)copper complexes were found to be dimeric dicationic products of the parent neutral complexes. These electro-crystallized ferrocenylethynyl materials could be a new entry to the family of ferroelectric materials [134-136]. The different shapes obtained by changing the chemical composition and stoichiometry present an approach to controlling the morphologies of the electro-deposited Cu-based microstructure, and are of high recent interest for fundamental studies and for potential applications in catalysis and other fields [129-132]. The ferrocenylethynyls have thus shown that they have enormous potential for further functionalization and hold promise for generating novel materials for scientific and technological development.
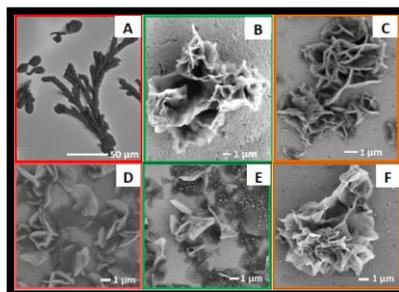
Figure 18. SEM images of electro-crystallized products from oxidation of complexes **86-91** (A-F). **86-88** Reprinted with permission from ref [127] and **89-91** from ref [128].
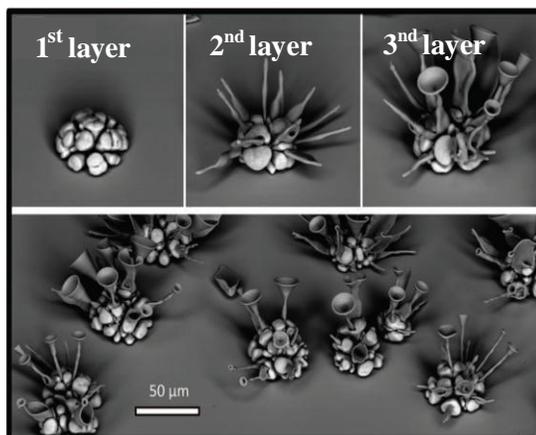
Figure 19. Layer by layer growth of crystal by changing the chemical composition. Reprinted with permission from ref [134].

4.   Present outlook and Future directions

Ferrocenylethynyl has been used widely as a platform for developing new materials, which have been investigated extensively over the past decade. This has allowed a thorough understanding of the structure-activity-function relationships of materials of this type, giving the inspiration to develop more advanced

materials for practical applications in the near future. While ferrocenyls are recognized redox-active molecules, examples presented in this review highlight the rich diversity of ferrocenylethynyl-based molecules and materials for numerous emerging applications. Connecting ferrocenylethynyl units to organic and inorganic structures provides a versatile approach for constructing new materials with novel properties.

The four types of connection of ferrocenylethynyl with diverse organic structures presented in this review have led to new catalyst systems, materials for sensors, pharmaceuticals, anti-cancer reagents, and precursor molecules for further coordination to metals and redox active complexes. A host of other molecules using the four types of connection could be synthesized which would be of interest to the new materials industries. Specifically, incorporation of photo- and thermally-active spacers such as azobenzenes in the bis(ferrocenylethynyl) complexes should prove very interesting as the azobenzene has the inherent property of switching between *cis-* and *trans*-conformation under the influence of an external applied field, leading to dual control over the new materials. Another novel approach presented here is the connection of ferrocenylethynyls to metal frames covalently and *via* coordination. The ferrocenyl units covalently connected to metal frames have shown improved conductivity and enhanced intra-molecular communication. Examples by Lu *et al.* have demonstrated an improvement in conductivity of the oligo-ynes on incorporation of ferrocene units. The coordination of functionalized ferrocenylethynyls have been shown to give electro-active clusters as demonstrated by Horikoshi *et al.* Shah *et al.* have recently shown that the new di- and tetra-ferrocenylethynylpyridinyl copper(I) halide complexes are conveniently accessible by coordination-driven self-assembly, and fascinating new materials have been produced by charge-driven electro-crystallization. These polynuclear complexes oxidize under mild conditions to form partially- or fully-oxidized electro-crystallized products. The inherent structural features based on the aromatic ring system and ethyne as well as metal cluster components potentially provide high electron-mobility, and therefore these crystalline materials with partially and fully occupied ferrocene electronic band structure will be of interest in future electronic materials and in optical components. The incorporation of PF_6^- into the structure can be considered as a "structurally well-defined" doping with implications for photo-excitation and electronic conductivity [137,138]. Furthermore, a combination of mobile electrons and structural rearrangements, which are possible in these novel materials, provides an entry into a new class of multi-ferroelectronics [134,139].

5. Acknowledgements

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