

# Click Chemistry: A Powerful and Versatile Methodology for Preparation of Ferrocene-Containing Polymers

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**Abstract** Ferrocene-containing polymers (FcPs) have attracted much research interest in the last decade, due to their unique properties and enormous applications. However, it is a great synthetic challenge to prepare FcPs before the advent of click chemistry. In this review, we summarized the recent research efforts on synthesizing FcPs through click reactions, which include click modification of preformed polymers and click polymerization of ferrocene (Fc) containing monomers. Due to the containing Fc moieties, the FcPs enjoy excellent redox activity, thermal stability, electrochemical property, and magnetism. Accordingly, they are promising to be used as electrochemical sensors, catalysts, magneto-ceramics, electrode modifiers, optical devices, etc.

**Keywords** Ferrocene-containing polymer · Click modification · Click polymerization

## 1 Introduction

Organometallic polymers (OMPs) have attracted much attention in the past decades due to their unique magnetic, electronic, optical, sensing and catalytic properties, and enormous applications in the areas of catalysts, magneto-ceramics, electrode modifiers, nonlinear optical devices, and electrochemical sensors, etc. [1–7]. Among the OMPs, ferrocene (Fc)-containing polymers (FcPs) are an important class [8–17]. Due to the ready availability, high stability, unique structure, and redox activity of Fc moiety, FcPs are drawing increasing interests in polymer science.

With enthusiastic efforts paid by polymer scientists, FcPs could be prepared by free radical, anionic, ring-opening, cyclotrimerization and condensation polymerizations [18–28]. Most of these polymerization techniques, however, should be carried out under harsh reaction conditions and careful exclusion of moisture and oxygen is necessary, which greatly limit their applications. Moreover, the post-modification of preformed polymers seems to be a good choice for the incorporation of Fc into the polymers. While, the introduction of reactive groups to the polymer chains is needed and efficient organic reactions are required for macromolecule reactions. Thus, efficient reactions applicable both in direct polymerization of Fc-containing monomers and post-functionalization of the preformed polymers by Fc groups are highly desirable.

The click chemistry well meets this requirement. Since it was conceptually proposed by Sharpless and co-workers in 2001 [29], click chemistry has greatly pushed the paces of chemistry. The Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) has been proven to be the archetypal click reaction [30–32]. Due to its remarkable advantages of high efficiency, mild reaction conditions, regio-selectivity, atom economy, and functional group tolerance etc., CuAAC has

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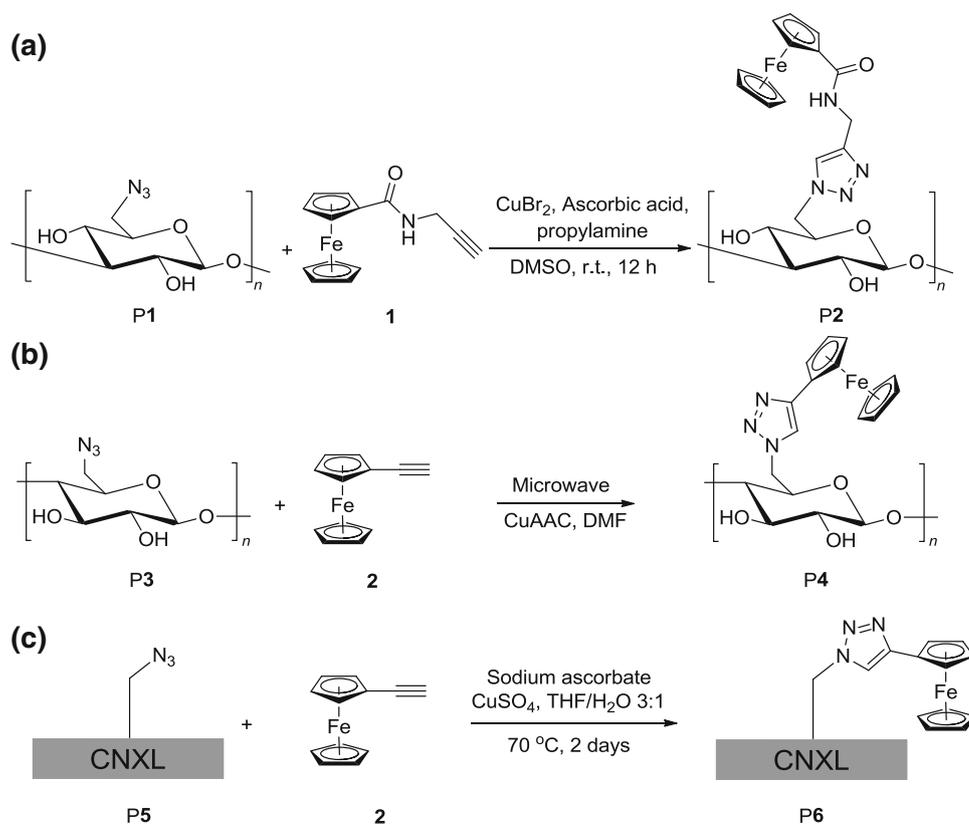
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**Scheme 1** Synthetic routes to Fc-containing polysaccharides through click modifications. CNXL cellulose nanocrystal



been widely utilized in polymer science especially in post-modification of preformed polymers [33–37].

Indeed, the powerful and versatile click reaction has been used for the synthesis of FcPs. However, to our best knowledge, there is no review summarizing the recent progress on this aspect. In this paper, we reviewed its progress and discussed the application of resultant FcPs.

## 2 FcPs Synthesized by Click Modification

### 2.1 Click Modification of Polysaccharides

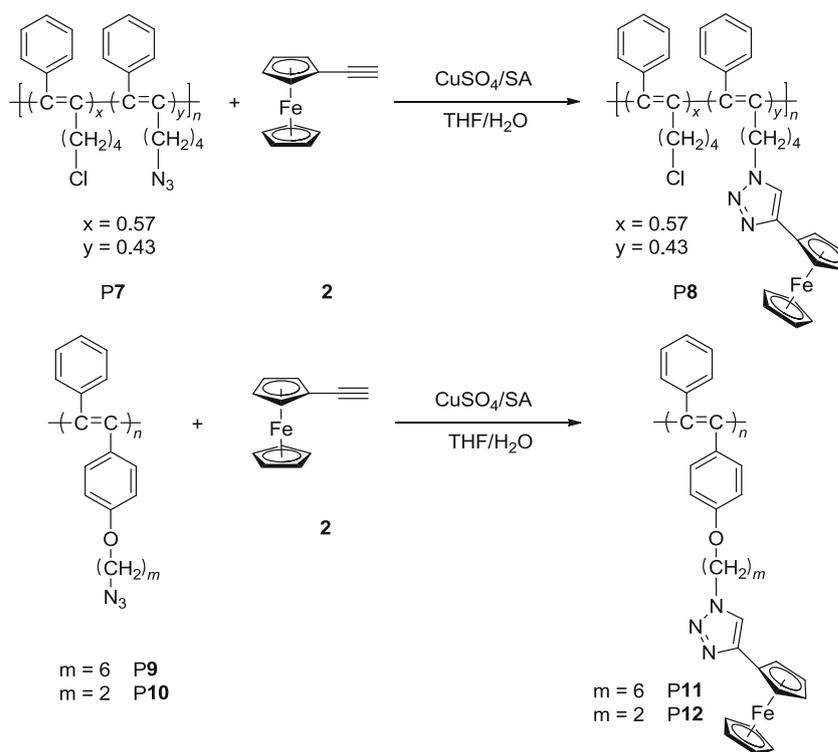
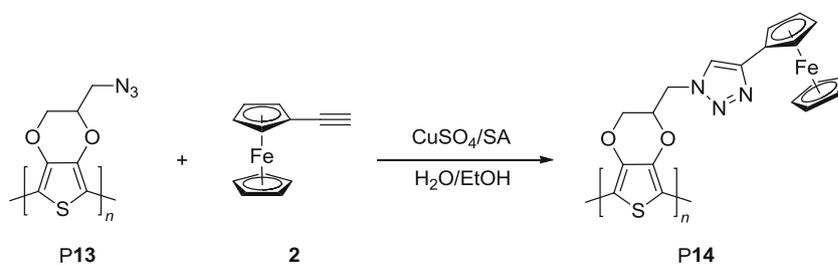
Polysaccharide-based materials are potential ‘eco-materials’ and have drawn much attention in material science. Due to the fast electron transfer, low oxidation potential, and two stable redox states of Fc group, the Fc-containing polysaccharides have potential applications in the areas of biosensor and bioelectrochemical systems. Obviously, the click modification of polysaccharides is an efficient way to prepare Fc-based polysaccharides.

In 2005, Shinkai et al. reported a successful example of attaching alkyne-terminated Fc modules (1) to a linear (1 → 3)-β-D-glucan of 6-azido-6-deoxy-curdlan (P1) through the click reaction (Scheme 1a). This reaction could finish in 1 h with good regio-selectivity (C-6 position).

Moreover, the redox-active ‘green’ material of Fc-containing (1 → 3)-β-D-glucan (P2) was obtained quantitatively [38]. Similarly, Ritter et al. synthesized Fc-decorated cellulose (P4) through the CuAAC between 6-azido-6-deoxy cellulose (P3) and ethynylferrocene (2) under the assistance of microwave (Scheme 1b). The host–guest complex between P4 and Rame-β-cyclodextrin (Rame-β-CD) was studied by 2D ROESY NMR and dynamic light scattering as well. In addition, the resultant Fc–CD complex is a redox-sensitive system which can be switched by electrochemical stimuli [39]. Using the Fc monomer of 2 and azide functionalized cotton-derived cellulose nanowhiskers (P5), Thielemans et al. prepared Fc-decorated cellulose nanocrystals (P6) in high yield (Scheme 1c). It is noteworthy that the charge-communication across the nanocrystal surface opens up the potential application of cellulose nanocrystals as a charge percolation template for the preparation of conducting films and bioelectrochemical devices [40].

### 2.2 Click Modification of General Polymers

The click modification strategy was also applied widely in decoration of other functional preformed polymers with Fc groups to endow them with redox activity, electrochemical property, magnetism, etc.

**Scheme 2** Click modification of disubstituted polyacetylenes by Fc groups. SA sodium ascorbate**Scheme 3** Synthetic route to Fc functionalized polythiophene P14

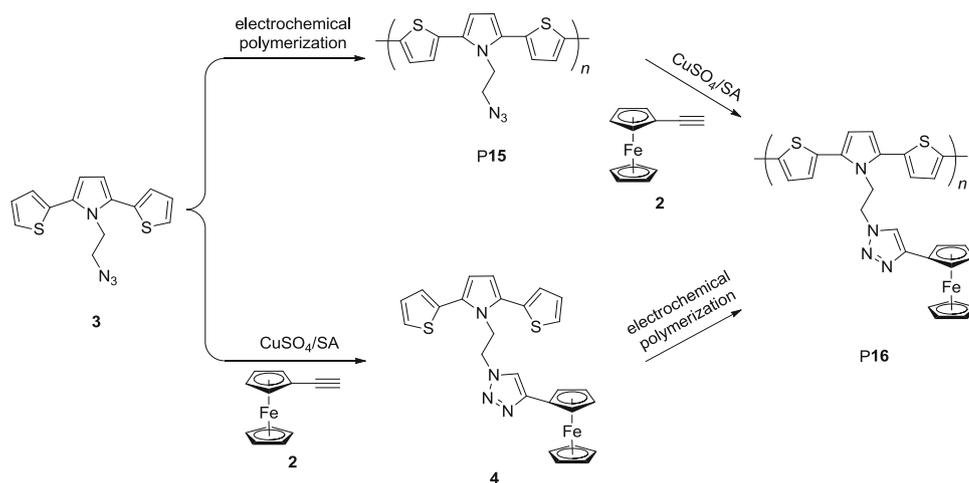
Our group reported an example of preparing Fc-based disubstituted polyacetylenes **P8**, **P11** and **P12** by click reactions of azido-functionalized disubstituted polyacetylenes **P7**, **P9** and **P10** with **2** (Scheme 2). The thermal stability and light refractivity of the modified polymers were enhanced compared to their precursors. Additionally, the polymers could be pyrolyzed to generate magnetic ceramics with high magnetic susceptibility [41, 42]. This work thus provides a general method to functionalize polyacetylenes with organometallic groups.

Polythiophene is another important kind of conjugated polymer. In 2009, Xian et al. reported the synthesis of Fc functionalized poly(3,4-ethylenedioxythiophene) (PEDOT-Fc) (**P14**) via the CuAAC (Scheme 3). The conducting polymer film of **P14** exhibited a relatively fast electron transfer rate and showed multi-color states when adjusting the applied potential [43]. The same reaction was used by Scavetta et al. to prepare PEDOT-Fc. They decorated the

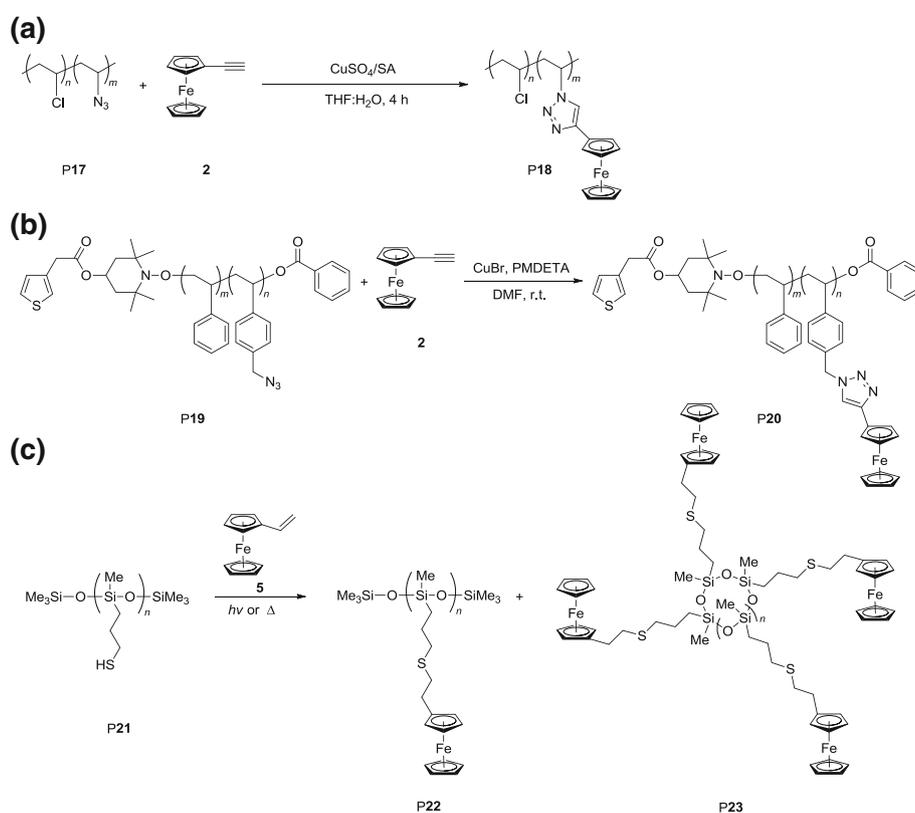
indium-tin-oxide (ITO) electrodes through electrodeposition of PEDOT-N<sub>3</sub> followed by CuAAC with **2**. Afterwards, the Fc-decorated electrode could be used as an amperometric sensor for the detection of dopamine with an average sensitivity of 196 mA M<sup>-1</sup> cm<sup>-2</sup>, and a limit of detection of 1 μM [44].

Another promising conducting polymer of poly(2,5-dithienylpyrrole) (PSNS) was also functionalized by Fc through CuAAC. As shown in Scheme 4, two strategies were used by Camurlu et al. to prepare Fc-containing PSNS. The first one is first electrochemical polymerization of 1-(2-azidoethyl)-2,5-di-thiophen-2-yl-1H-pyrrole (**3**) to yield PSNS-N<sub>3</sub> (**P15**) films on ITO electrodes. Afterward, the PSNS-N<sub>3</sub> coated ITO electrode was reacted with **2** in the presence of CuSO<sub>4</sub> and sodium ascorbate, and the PSNS-Fc (**P16**) coated electrode was obtained with potential usages as electrocatalysts, biosensors, and gas sensors [45]. Another strategy is first to perform the

**Scheme 4** Different synthetic routes to Fc-containing PSNS P16



**Scheme 5** Click modification of commodity polymers by ferrocene modules. PMDETA = *N,N,N',N'',N'''*-pentamethyldiethylenetriamine

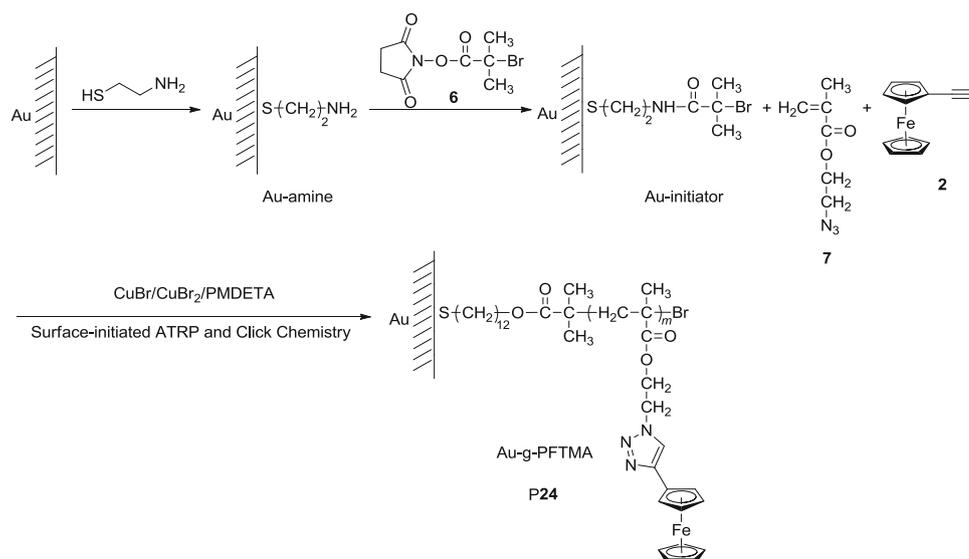


CuAAC of **3** and **2**, then electrochemically polymerized the precursor monomer of SNS-Fc (**4**), and PSNS-Fc films on ITO electrodes were finally prepared [46]. Additionally, a copolymer P(SNS-Fc-co-EDOT) was obtained by electropolymerization of 3,4-ethylenedioxythiophene (EDOT) and SNS-Fc. The experimental results imply that both PSNS-Fc and P(SNS-Fc-co-EDOT) hold high potential for the fabrication of electrochromic devices.

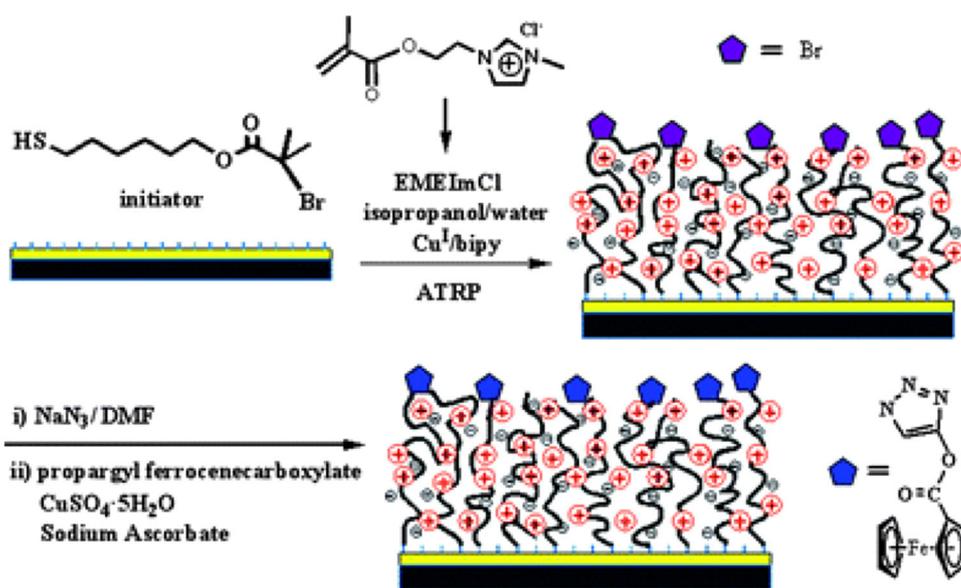
Besides the aforementioned conjugated polymers, the commodity polymers such as poly(vinyl chloride) (PVC),

polystyrene (PS), and polysiloxane were also post-functionalized with Fc groups via the click reactions (Scheme 5) [47–49]. For example, the Fc functionalized PVC (**P18**) membranes, reported by Bakker et al., exhibit the potential as solid state voltammetric ion sensors [47]. Moreover, Yilmaz et al. efficiently incorporated Fc moieties into the PS as pendants (**P20**) via CuAAC, which could act as a chemical probe to detect phosphate anions [48]. Furthermore, Cuadrado et al. reported the synthesis of Fc functionalized polymethylsiloxane (**P22**, **P23**) via thiol–ene

**Scheme 6** Click modification of Au surface grafted with polymer brushes. Reproduced with permission from Ref. [54]. Copyright 2010, American Chemical Society



**Scheme 7** Preparation procedure of Fc-terminated polyelectrolyte brushes on Au surface. Reproduced with permission from Ref. [51]. Copyright 2009, Royal Society of Chemistry

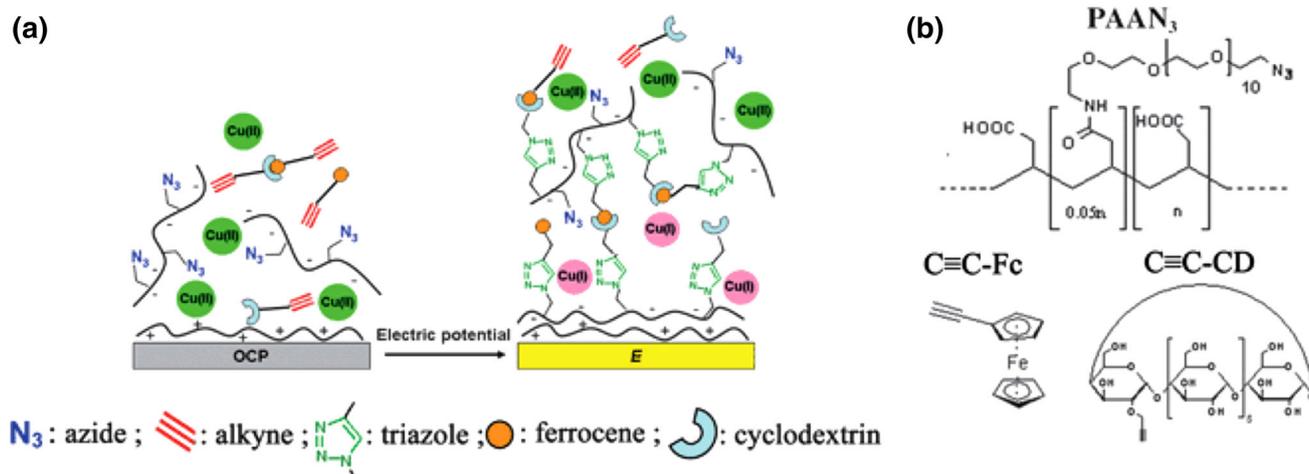


click chemistry for the first time. The thermal stability of P22 and P23 was significantly improved by the incorporation of Fc groups. P22 and P23 could be used to modify the Pt or Au electrode surfaces, and endow them with a stable redox reaction over long periods of time [49].

### 2.3 Click Modification of Functional Polymeric Surfaces

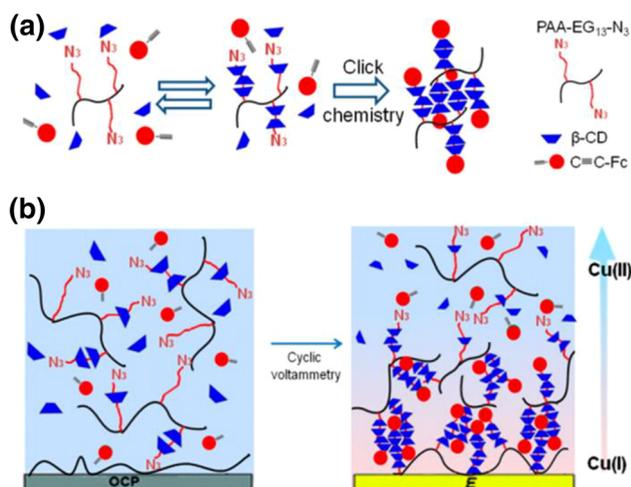
The modification of surfaces by polymers or polyelectrolytes has received considerable attention over the last few years. For example, Fc-based polymer brushes grafted on solid substrates have been employed for the development of electro-active and electro-catalytic films,

electrochemical DNA sensors, and amperometric biosensors [50–53]. Fu et al. reported a gold substrate with surface-grafted Fc-based polymer brushes (Au-g-PFTMA) (P24), which was prepared by combination of surface-initiated atom transfer radical polymerization (SI-ATRP) and CuAAC in one pot (Scheme 6) [54]. A similar strategy was implemented by Zhou et al. [51]. They prepared Fc-terminated polyelectrolyte brushes on a gold surface through three step procedures consisting of SI-ATRP,  $\text{NaN}_3$  substitution, and CuAAC (Scheme 7). The electrochemical property and electro-catalytic behaviours of these Fc-terminated polyelectrolyte brushes are responsive to external stimuli, enables it to be developed into smart surfaces with switchable gating properties.



**Scheme 8** Schematic representation of the self-construction of PAA films using electrochemically triggered click chemistry and host-guest interactions. *OCP* open circuit potential, *E* electric potential.

They represent the potential applied on the electrode. Reproduced with permission from Ref. [55]. Copyright 2012, Royal Society of Chemistry



**Scheme 9** Electro-triggered click chemistry to construct the PRX film at the surface of the electrode. *OCP* open circuit potential, *E* electric potential, they represent the potential applied on the electrode. Reproduced with permission from Ref. [56]. Copyright 2013, American Chemical Society

Interestingly, Schaaf et al. introduced a concept of onepot morphogen-driven film building-up for surface modification [55]. Dialkyne linkers were first formed through the host-guest interaction between Fc and cyclodextrin (CD). A poly(ethylene imine) coated electrode was used to anchor azide decorated poly(acrylic acid) (PAAN<sub>3</sub>) blocks by electrostatic attraction. Afterward, with the assist of electrochemical stimulus, the azide-alkyne click reaction can be catalysed by Cu(II), which allows the continuous self-construction of a film (Scheme 8). The properties of the resulting film can be facilely modulated by influencing

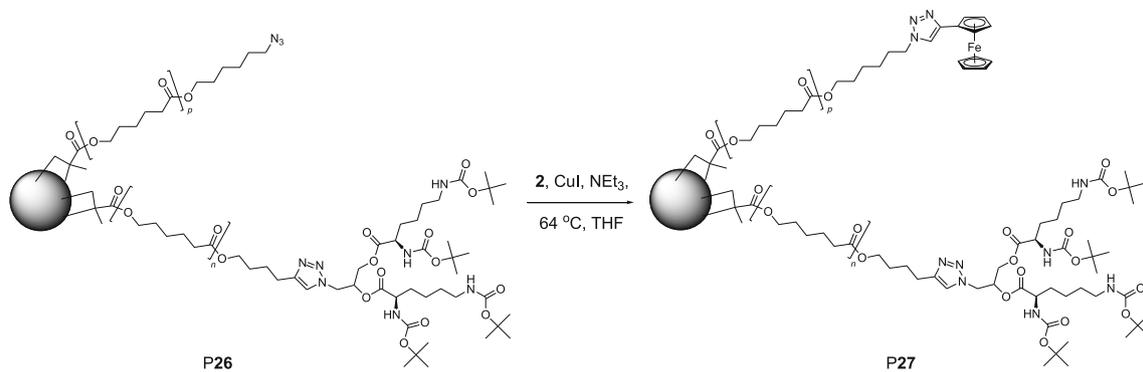
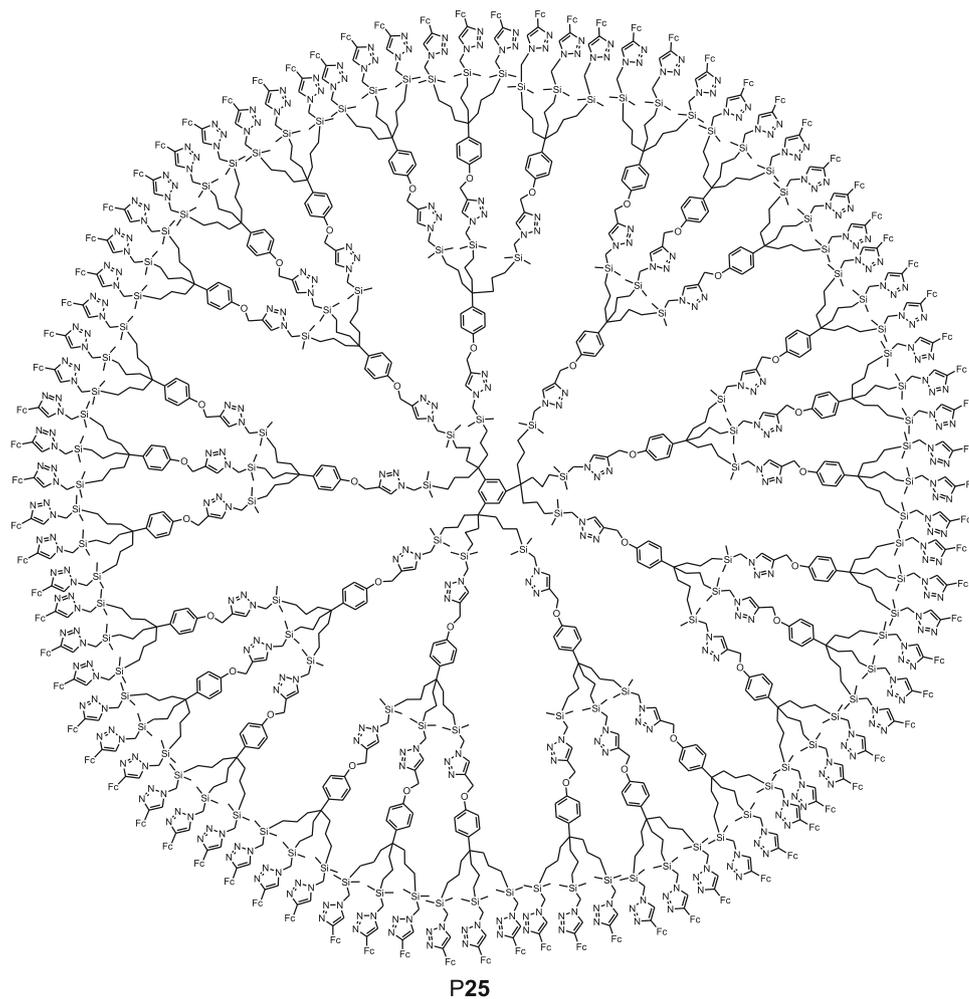
the click reaction or the host-guest interaction involved. For example, the use of excess CD blocks would produce films with empty CD units which allow immobilization of other guest molecules and thus functionalization of the film. Similar strategy was adopted by Boulmedais et al. for the construction of Fc-containing nanometric size films based on polyelectrolytes and polyrotaxane (PRX) assemblies (Scheme 9) [56]. The Fc-containing film exhibits high stability to electric stimulus.

#### 2.4 Click Modification of Topological Polymers

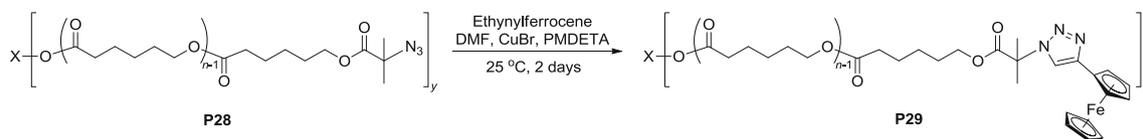
Dendrimers are well-defined macromolecules with highly branched and globular architectures. The tremendous reactive groups on their peripheries could endow them with additional function via the post-reactions. Astruc et al. showed an example of preparation of Fc-functionalized dendrimer P25 using post click reaction (Chart 1) [57–62]. P25 exhibits the unique property of electrochemically selective recognition of oxo anions (adenosine triphosphate ATP<sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and HSO<sub>4</sub><sup>-</sup>) and transition-metal cations (Cu<sup>+</sup>, Cu<sup>2+</sup>, Pd<sup>2+</sup>, and Pt<sup>2+</sup>). Furthermore, due to the strong binding ability of palladium cations with triazoles in P25, the authors also prepared various dendrimer-encapsulated Pd nanoparticles with a pre-organized number of Pd atoms, which could be used as catalysts [58, 59].

The Fc-functionalized topological polymers could also be prepared by combining the ring-opening and click reactions [63, 64]. Hvilsted, Yilmaz et al. reported such examples, respectively. Hvilsted and coworkers prepared miktoarm cored cross-linked star copolymers consisting of Fc-terminated and *L*-lysine dendritic arms (Scheme 10) [63]. Whereas, Yilmaz and coworkers synthesized Fc-terminated

**Chart 1** Structure of the Fc-containing dendrimer P25

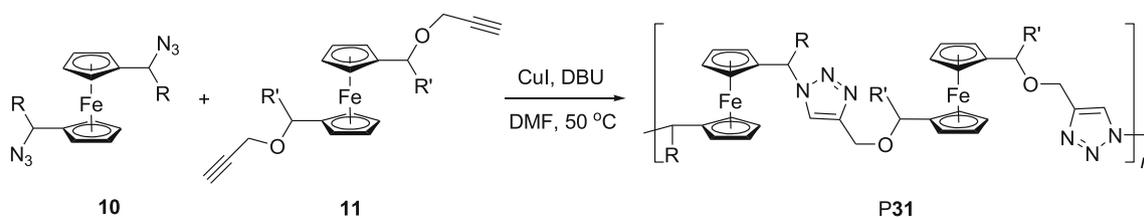
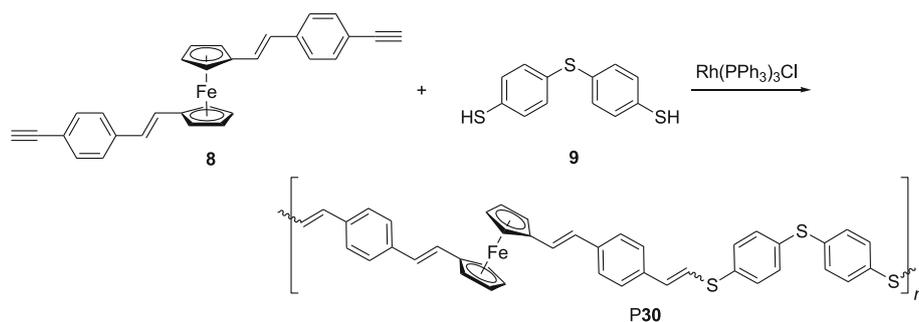


**Scheme 10** Synthesis of Fc-containing miktoarm core-crosslinked star copolymers



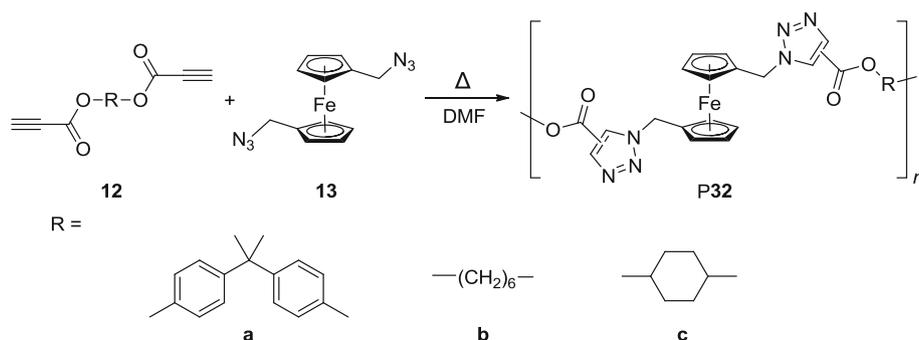
**Scheme 11** Synthetic route to star-shaped polymers with Fc end-capped PCL arms

**Scheme 12** Synthesis of Fc-containing PVS by click polymerization of diyne **8** and dithiol **9**



**Scheme 13** Synthesis of Fc-containing PTAs by AACPs of diynes **11** and diazides **10**. *DBU* 1,8-diazabicyclo[5.4.0]undec-7-ene

**Scheme 14** Synthesis of Fc-based PACTs by metal-free AACPs of dipropiolates **12** and diazide **13**



linear and star-shaped poly( $\epsilon$ -caprolactone)s (PCLs) (**P29**) with different numbers of arms (Scheme 11). Due to their electrochemical activity, **P29** could be potentially applied in DNA sensing [64].

### 3 FcPs Synthesized by Click Polymerization

Although the click modification of pre-formed polymers is a facile and efficient way for the preparation of FcPs, the pre-polymers have to be synthesized by traditional polymerization techniques like free-radical, ring-opening, and electrochemical polymerizations, etc. These techniques are, however, complicated and tedious. Therefore, the development of direct and simple synthetic approaches to prepare FcPs is highly desirable.

The robust and orthogonal click polymerization, developed based on the click reaction, is an ideal alternative for the preparation of FcPs. Our group has succeeded in preparation of FcPs via click polymerizations. The

$\text{Rh}$ -catalyzed thiol–yne click polymerization of (*E,E*)-1,1'-bis[2-(4-ethynylphenyl)vinyl]ferrocene (**8**) and 4,4'-thiodibenzenethiol (**9**) readily produced regioregular Fc-containing poly(vinylene sulfide) (PVS) (**P30**) in high yields (up to 85.6 %) (Scheme 12) [65]. **P30** possesses better thermal stability and higher light refractive index than other reported PVSs, owing to the containing Fc moieties. Furthermore, **P30** displays superior optical limiting property over  $\text{C}_{60}$  and could serve as a precursor to prepare semiconducting  $\text{Fe}_7\text{S}_8$  ceramic.

The  $\text{Cu}(\text{I})$ -catalyzed azide–alkyne click polymerization (AACP) was employed to prepare FcPs as well. As demonstrated by Barner-Kowollik et al., the  $\text{Cu}(\text{I})$ -catalyzed AACP of Fc-containing diazides and diynes readily furnished Fc-containing polytriazoles (PTAs) (**P31**) with high molecular weights ( $M_w$  up to  $78\,000\text{ g mol}^{-1}$ ) in 6 h (Scheme 13) [66].

Although the Fc group is biocompatible, the  $\text{Cu}$  catalyst is toxic. The removal of the copper residues after  $\text{Cu}(\text{I})$ -catalyzed AACP is, however, difficult. To surmount this

difficulty, we have successfully established the metal-free AACPs of activated alkynes and azides [67–73]. Recently, we employed the metal-free AACP of propiolates and azide to prepare Fc-containing poly(aroxycarbonyltriazole)s (PACTs) [74]. As shown in Scheme 14, heating of the mixture of propiolates (**12**) and 1,1'-bis(azidomethyl)ferrocene (**13**) in DMF at 80 °C for 24 h readily produced PACTs (**P32**) with molecular weights up to 13 400 g mol<sup>-1</sup> and fraction of 1,4-isomer higher than 87.7 % in high yields (92.7–96.9 %). It is noteworthy that this polymerization proceeded smoothly in air without excluding oxygen and moisture. **P32** are redox active and could be used as precursors to generate soft magnetic ceramics with high magnetic susceptibility and low coercivity when pyrolyzed at elevated temperature.

#### 4 Summary and Perspective

In this review, we summarized the recent progress on synthesizing FcPs by click reactions. The FcPs could be obtained through click modification of preformed polymers such as polysaccharides, polyacetylenes, polythiophenes, PVC, PS, polysiloxane, functional surfaces, and topological macromolecules. Moreover, such polymers could also be produced by directly polymerizing Fc-containing monomers via the thiol–yne, azide–alkyne click polymerizations. Due to their containing Fc moieties, the resultant FcPs enjoy good redox activity, thermal stability, electrochemical property, and magnetism, thus have enormous applications in such areas as electrochemical sensors, catalysts, magneto-ceramics, electrode modifiers, optical devices.

Although the research in this area progresses rapidly, many possibilities are still waiting for exploration. Future directions and endeavours in the area include the development of new and facile click reactions and click polymerizations to efficiently synthesize FcPs, and exploration of novel functions and new applications of resultant FcPs.

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