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2023, 7, 4967Synthetic styrene-based bioinspired model of the
[FeFe]-hydrogenase active site for electrocatalytic
hydrogen evolution†Afridi Zamader,^{‡ab} Bertrand Reuillard,^{ID *a} Julien Pérard,^a Laurent Billon,^{ID c}
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Integration of molecular catalysts inside polymeric scaffolds has gained substantial attention over the past decade, as it provides a path towards generating systems with enhanced stability as well as enzyme-like morphologies and properties. In the context of solar fuels research and chemical energy conversion, this approach has been found to improve both rates and energy efficiencies of a range of catalytic reactions. However, system performance still needs to be improved to reach technologically relevant currents and stability, parameters that are heavily influenced by the nature of the incorporated molecular catalyst. Here, we have focused on the integration of a biomimetic $\{\text{Fe}_2(\mu\text{-adt})(\text{CO})_6\}$ ($-\text{CH}_2\text{NHCH}_2\text{S}-$, azadithiolate or adt^{2-}) based active site ($[\text{2Fe2S}]^{\text{adt}*}$), inspired by the catalytic cofactor of [FeFe] hydrogenases, within a synthetic polymeric scaffold using free radical polymerization. The resulting metallopolymer $[\text{2Fe2S}]^{\text{adt}*}_k[\text{DMAEMA}]_l[\text{PyBMA}]_m$ (DMAEMA = dimethylaminoethyl methacrylate as water soluble monomer; PyBMA = 4-(pyren-1-yl)-butyl methacrylate as hydrophobic anchor for heterogenization) were found to be active for electrochemical H_2 production in neutral aqueous media. The pyrene content was varied to optimize durability and activity. Following immobilization on multiwalled carbon nanotubes (MWNT) the most active metallopolymer, containing ~ 2.3 mol% of PyBMA, could reach a turnover number for hydrogen production (TON_{H_2}) of $\sim 0.4 \times 10^5$ over 20 hours of electrolysis at an overpotential of 0.49 V, two orders of magnitude higher than the isolated catalyst counterpart. The study provides a synthetic methodology for incorporating catalytic units featuring second coordination sphere functional groups, and highlights the benefit of the confinement within the polymer matrix for catalytic performance.

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Introduction

Water electrolysis powered by renewable energy is one of the most sustainable methods to produce clean H_2 .¹ Current electrolyzer technologies still rely on the use of expensive platinum-group metals (PGMs) based cathodes for proton reduction.^{2–4} In order to overcome this issue, the development of efficient noble-metal free H_2 production catalysts is required.^{5,6}

In nature, [FeFe]-hydrogenase enzymes are capable of H_2 production at high catalytic rates ($\sim 10^4$ moles of H_2 per mole of enzyme per second) with negligible overpotential requirement

at neutral pH using only earth-abundant metals.⁷ Their remarkable activities are enabled by a hexa-nuclear iron cofactor denoted the “H-cluster”.⁸ The latter consists of a $[\text{4Fe-4S}]$ cluster, coupled to a diiron active site ($[\text{2Fe}]_{\text{H}}$) where the catalysis takes place. The Fe ions of $[\text{2Fe}]_{\text{H}}$ are each coordinated by one terminal CO ligand and one terminal CN^- ligand, and a third CO ligand bridges the two ions.⁹ The two Fe ions in $[\text{2Fe}]_{\text{H}}$ are further bridged by an azadithiolate ($-\text{SCH}_2\text{NHCH}_2\text{S}-$, adt^{2-}) ligand, in which the bridgehead amine is critical for efficient proton delivery during catalysis.^{10–13} In recent years, these fascinating biomolecules have been extensively studied on electrode surfaces and their potential application in “bio-hybrid devices” investigated.^{14–16} In parallel, [FeFe]-hydrogenases have served as blueprints for the development of molecular bioinspired catalysts.^{7,17–22} In particular, extensive efforts have been invested in $[\text{2Fe}]_{\text{H}}$ models of the general structure $\{\text{Fe}_2(\mu\text{-SR})_2(\text{CO})_6\}$ (RS^- = thiolate ligand).^{7,23} Nevertheless, few catalysts in this di-iron family have been reported to display substantial activities when heterogenized on electrodes or incorporated within synthetic macromolecular chains mimicking proteins. A wide range of strategies have been

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reported in the literature by Darensbourg *et al.*,^{24,25} Talarmin *et al.*,²⁶ Artero *et al.*,²⁷ Pickett *et al.*,²⁸ Liu *et al.*^{29–31} targeting immobilization at carbon-based or metal electrodes *via* covalent grafting or simple physisorption. However, most of these systems showed rapid loss of activity either following the degradation of the linkage or the active sites. More recently Dey and coworkers reported exceptional improvements in the activity of immobilized $\{\text{Fe}_2(\mu\text{-adt})(\text{CO})_6\}$ based complexes,^{32–34} following physisorption^{32,33,35,36} and covalent grafting³⁴ on edge plane graphite (EPG) electrodes in aqueous media. However, both strategies yielded relatively low catalyst loadings (lower than 1 nmol cm^{-2}). Recently, our groups demonstrated the simple and efficient immobilization of a pyrene containing naphthalene bridged $\{\text{Fe}_2(\mu\text{-SR})_2(\text{CO})_6\}$ complex on multiwalled carbon nanotubes (MWNT).³⁷ The presence of pyrene enabled catalyst immobilization through π - π interactions, resulting in a largely improved surface loadings (up to 9.5 nmol cm^{-2}) and excellent stability of the anchoring group on the electrode during electrolysis at neutral pH. However, the latter system displayed moderate activity due to the degradation of the active site during catalysis.³⁷

In parallel, the integration of such diiron based complexes within organic polymer scaffolds has emerged as a promising approach to improve their stability and catalytic properties.^{38–43} Among such metallopolymers, Brezinski *et al.* reported a striking example with the integration of a naphthalene bridged $\{\text{Fe}_2(\mu\text{-SR})_2(\text{CO})_6\}$ complex inside a poly-(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) polymeric scaffold. The resulting metallopolymer $[2\text{Fe}2\text{S}]\text{-PDMAEMA}$ showed excellent activities at neutral pH under homogeneous conditions.^{42,43} These outstanding activities were rationalized by the presence of the PDMAEMA which was proposed to provide not only water solubility but also ensuring efficient proton transfer during catalysis as a polybase. We could further demonstrate that redesigning of the aforementioned metallopolymers to include a pyrene anchoring group, yielding $[2\text{Fe}2\text{S}]\text{-P}(\text{DMAEMA-}r\text{-PyBMA})$ (PyBMA = 4-(pyren-1-yl)-butyl methacrylate) afforded a system showing high electrocatalytic H_2 production activities at neutral pH once immobilized at MWNT based electrodes.⁴⁴ However, the catalytic performance of the latter system was limited by the steady degradation of the diiron catalyst over the course of the electrolysis.

In this study, we explored the possibility of improving the performance of such pyrene containing metallopolymers for electrochemical H_2 production through the re-design of the diiron catalyst “active site”. More specifically, we strived to incorporate a potentially more robust catalytic core within the polymer based on previously reported molecular designs,^{32,33} and we report the successful integration of a $\{\text{Fe}_2(\mu\text{-adt})(\text{CO})_6\}$ based catalyst within a polymer scaffold combining both DMAEMA and PyBMA co-monomer units *via* free radical polymerization using azobisisobutyronitrile (AIBN). To the best of our knowledge, this is the first report of a $\{\text{Fe}_2(\mu\text{-adt})(\text{CO})_6\}$ derivative active site successfully incorporated within a multi-functional synthetic macromolecular chain. The resulting original metallopolymers were active for H_2 production at neutral pH (Fig. 1A). The influence of the polymer scaffold was

elucidated by comparing the activity of the metallopolymers to that of a molecular pyrene modified isolated analogous diiron catalyst.

2. Results and discussion

2.1. Synthesis and characterization

Efforts to incorporate $[\text{Fe}_2(\mu\text{-SCH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4\text{CHCH}_2)\text{CH}_2\text{S})](\text{CO})_6$ (**1** or $[2\text{Fe}2\text{S}]^{\text{adt}}$) (Fig. 1A) inside a styrene based polymeric scaffolds through reversible addition-fragmentation chain-transfer (RAFT) polymerization have been reported.⁴⁵ However, those attempts failed at synthesis stage, possibly due to poor stability of the diiron core under the employed conditions. Thus, we employed a synthetic route proceeding *via* a free radical polymerization reaction in the presence of AIBN without any RAFT reagent. For that, complex **1** and PyBMA, were synthesized following previously reported protocols.^{44,45} Subsequently, complex **1**, PyBMA and commercially available DMAEMA were used as co-monomers to synthesize the metallopolymers with AIBN as initiator in toluene at 70°C for 12 hours (Scheme S1†). The pyrene component ensures efficient binding to MWNT, but can result in unwanted radical termination reactions during polymerisation and impair the hydrophilicity of the polymer.⁴⁴ Thus three different metallopolymers *i.e.*, $[2\text{Fe}2\text{S}]^{\text{adt}}_k[\text{DMAEMA}]_l[\text{PyBMA}]_m$ were prepared, denoted **1a**, **1b** and **1c** incorporating different molar equivalents of PyBMA with respect to that of DMAEMA in the feed media (1%, 5% and 10% in **1a**, **1b** and **1c**, respectively, Fig. 1A and Scheme S1†) (see ESI† for details). Here *k*, *l* and *m* represent the molar ratios between $[2\text{Fe}2\text{S}]^{\text{adt}}$, DMAEMA and PyBMA, respectively. As reference, an “isolated” diiron site, denoted as $[2\text{Fe}2\text{S}]^{\text{adt}}\text{-Py}$ or complex **2**, was synthesized (Scheme S2†). Complex **2** incorporates a pyrene anchoring unit but lacks the polymeric scaffold, allowing us to distinguish the influence of the polymeric framework on the electrocatalysis (Fig. 1A). We note that it is unlikely that the amine from adt^{2-} solely acts as secondary coordination sphere proton shuttle as the latter requires *meta* substitution of the aniline moiety, as reported earlier.^{35,46}

The synthesized compounds (*i.e.*, metallopolymers **1a–c** and complex **2**) were characterized using a range of spectroscopic techniques. In all three metallopolymers, the ^1H NMR exhibited peaks between 7.0–7.3 ppm due to the aromatic group present at amine bridgehead of the diiron active site. Compared to spectra collected for complex **1** (Fig. S1†), **1a–c** showed negligible shifts in peak positions which suggest that the polymerization did not cause significant changes in the electronic distribution at the metal center. In addition, **1a–c** showed broad peaks between 7.8–8.4 ppm, characteristic of pyrene, and multiple peaks in the aliphatic region (0–5 ppm), originating from DMAEMA (Fig. S2–S5†). Integration of the previously mentioned signature peaks allowed to calculate the ratio between each co-monomer (*k*:*l*:*m*), as shown in Table 1, and estimate the composition of the metallopolymers' backbones. This analysis indicated the presence of ~ 0.9 , ~ 2.3 and $\sim 6.6 \text{ mol\%}$ of pyrene in **1a**, **1b** and **1c** respectively (Table 1). As expected, the ^1H NMR spectrum of the complex **2** revealed distinct peaks ranging from 3.5 to 5.5 ppm, 7.2 to 7.9 ppm, 8.0



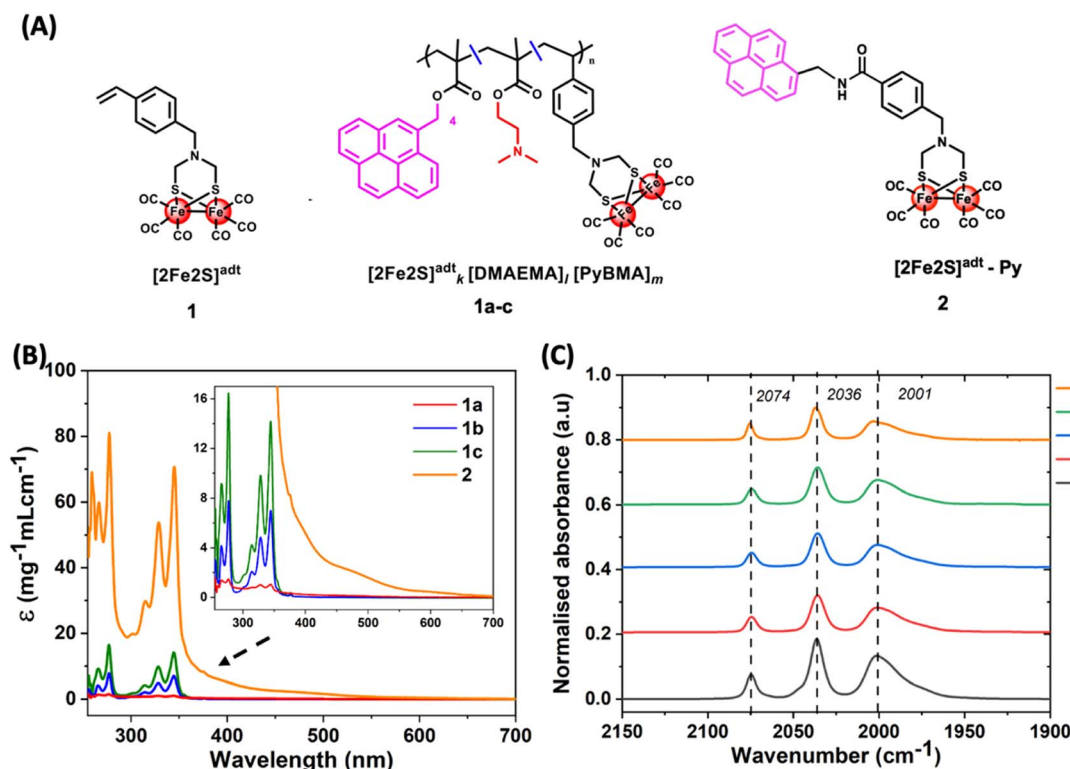


Fig. 1 (A) Schematic representation of synthesized compounds, i.e., complex 1 (synthetic precursor of the metallopolymer), metallopolymer 1a–c and complex 2, (B) UV-vis spectra of 1a–c (197; 50 and 20 $\mu\text{g mL}^{-1}$) and 2 (11 $\mu\text{g mL}^{-1}$) in DMF (C) Infrared spectroscopy of 1, 1a–c and 2 in CHCl_3 using transmission mode. The intensity of FTIR traces of 1a were multiplied by 3 and 1b and 1c multiplied by 10 each to have between comparison with 1 and 2. Here $k : l : m$ is the ratio of $[\text{2Fe2S}]^{\text{adt}} : [\text{DMAEMA}] : [\text{PyBMA}]$. The exact details of the ratio for each metallopolymer were mentioned in Table 1.

to 8.5 ppm, attributable to the protons present on the aliphatic, bridgehead aromatic and pyrene groups, respectively (Fig. S7†).

UV-vis spectroscopy further supported the presence of the pyrene in both the metallopolymer 1a–c and complex 2 by showing multiple sharp peaks between 255–355 nm attributed to the pyrene group (Fig. 1B). As the relative pyrene content in 2 is much larger compared to 1a, 1b and 1c, a noticeable enhancement of the intensity of the corresponding pyrene peaks was observed. Infrared spectroscopy allowed to clearly observe the CO stretching bands at 2074, 2036 and 2001 cm^{-1} , confirming the presence of the organometallic active site inside the polymers (Fig. 1C). The peak positions were identical to those observed for complex 1, again indicating that the polymer had negligible effects on the electronic structure of the di-iron

complex, in agreement with the ^1H NMR data. Calibrating the absorbance of these infrared bands with that of complex 1 revealed the presence of ~ 1.6 active sites per mol of 1a and ~ 1 active site per mol of both 1b and 1c (Fig. S10, S11 and Table S2†). In addition, a strong peak at 1726 cm^{-1} was observed for all polymers, attributable to carbonyls from the ester groups present in the polymeric backbone, as expected this band was not present in the precursor 1 (Fig. S12†).⁴⁴ The DMAEMA groups in this type of metallopolymer have been previously shown to have a $\text{p}K_{\text{a}}$ of ≈ 8.4 .⁴³ To further elucidate the protonation chemistry of 1a–c, the basicity of the adt-amine in the metallo-polymers was probed using 1b as a representative model, utilizing attenuated total reflection ATR-FTIR spectroscopy. It has been previously reported that below pH 4.4 in

Table 1 Quantitative analysis of all metallopolymer

Metallopolymer or complex	DMAEMA (<i>l</i>)/PyBMA (<i>m</i>)/diiron site (<i>k</i>) final molar ratio ^a	mol% of PyBMA	Fe content ^b ($\text{mg}_{\text{Fe}} \text{g}_{\text{pol}}^{-1}$)	M_{n}^c (g mol^{-1})	$\mathcal{D}^c$
1a	37/0.35/1	0.9	9.6 ± 0.2	14 200	2.7
1b	62/1.5/1	2.3	4.10 ± 0.06	16 650	2.19
1c	53/3.8/1	6.6	4.0 ± 0.1	17 300	2.25
2	—	—	0.16 ± 0.01	—	—

^a Calculated from ^1H NMR spectrum. ^b Measured by ICP-OES. ^c M_{n} = molecular weight of the metallopolymer and $\mathcal{D}$ = dispersity, both measured by SEC.



aqueous media, and under strong acidic condition in organic media, the bridgehead amine of $\text{Fe}(\mu\text{-adt})(\text{CO})_6$ and closely related complexes begin to undergo protonation, resulting in a distinct hypsochromic shift of 20 cm^{-1} in the stretching band of CO ligands coordinated to Fe.^{46–48} Interestingly, within the pH range of 2 to 8, no obvious shift of the CO bands is observed, indicating that the bridgehead amine remains in deprotonated state. However, at pH 0, a marginal hypsochromic shift of 3 to 8 cm^{-1} was noticed (Fig. S13†). To identify the origin of the latter shift, a comparative study was carried out using a similar metallopolymer, $[\text{2Fe2S}]\text{-P(DMAEMA-}r\text{-PyBMA)}$,⁴⁴ where the active site lacks the bridgehead amine. The results revealed that the later metallopolymer exhibited only a minor $1\text{--}2\text{ cm}^{-1}$ hypsochromic shift in the CO bands when transitioning from pH 7 to pH 0 (Fig. S14†). This finding suggests that observed shift ($3\text{--}8\text{ cm}^{-1}$) for **1b** could be due to the protonation of the bridgehead nitrogen at pH 0, albeit we note that the shift is unusually small.

Complex **2** also exhibited the expected carbonyl ligand bands, with wavenumbers of 2075 , 2037 , and 2002 cm^{-1} along with a weak carbonyl stretching band at 1659 cm^{-1} attributed to the presence of the amide bond (Fig. 1C and S15† orange trace). Inductively coupled plasma optical emission spectrometry (ICP-OES) was further employed to quantify the concentration of Fe in the polymers and $9.6 \pm 0.2\text{ mg}$ of Fe per gram polymer ($\text{mg}_{\text{Fe}}\text{ g}_{\text{pol}}^{-1}$) was estimated for **1a** while 4.10 ± 0.06 and $4.0 \pm 0.1\text{ mg}_{\text{Fe}}\text{ g}_{\text{pol}}^{-1}$ were estimated for **1b** and **1c**, respectively. The discrepancy between the Fe content estimated by NMR relative to the ICP quantification (about 36–55% of expected Fe could be detected in ICP) can be rationalized by the relatively small NMR signals used for the quantification. However, degradation of a small fraction of the Fe–CO core during the polymerization reaction cannot be fully excluded, as previously proposed.⁴⁵ Similarly, complex **2** exhibited $0.16 \pm 0.01\text{ g}$ of Fe per gram of complex, within the error margin of the expected value (0.15 g of Fe per gram of complex). Size exclusion chromatography (SEC) of metallopolymer **1a–c** showed that the molecular weight varied between $14\,200\text{--}17\,300\text{ g mol}^{-1}$ with dispersity (D) ranging from 2.2 to 2.7. The dispersity values indicate a degree of length inhomogeneity in the metallopolymer (*i.e.* $D > 1$), which can be ascribed to the nature of the employed polymerization method, *i.e.*, free radical polymerization (Fig. S16,† and Table 1). The combination of ICP-OES and SEC data also provides a second measure of active site incorporation, suggesting ~ 1.2 active sites per mole for **1a** and ~ 0.6 active sites per mole of both **1b** and **1c**, in line with the estimates from infrared spectroscopy discussed above (Tables 1 and S2†).

2.2. Electrochemical assessments

2.2.1. Homogeneous electrochemistry. The electrochemical properties of the synthetic precursor complex **1**, pyrene modified diiron site complex **2** and metallopolymer **1a–c** were first studied in organic media. Cyclic voltammetry (CV) studies of complex **1** showed a quasi-reversible redox event at $E_{1/2} = -1.55\text{ V vs. Fc}^{+/0}$ ($E_{\text{p,c}} - E_{\text{p,a}} = \Delta E_{\text{p}} = 130\text{ mV}$) whereas both complex **2** and the metallopolymer displayed an irreversible

cathodic wave located at -1.56 V and between -1.62 to $-1.65\text{ V vs. Fc}^{+/0}$, respectively (Fig. S17 and S18†). These redox processes were assigned to an Fe based one-electron redox process ($\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{I}}\text{Fe}^0$) in agreement with previous reports on closely related diiron active sites.^{33,49,50} In contrast to **1** and **2**, **1a–c** are soluble in water due to the presence of DMAEMA units in the conjugated macromolecular chain. Therefore, the electrocatalytic activities of the metallopolymer were further assessed in aqueous media (0.2 M sodium phosphate buffer, pH 7) at a glassy carbon electrode (GCE). Under these conditions, **1a–c** displayed a single irreversible reduction process with an onset potential of -0.34 to -0.36 V vs. RHE attributed to the electrocatalytic reduction of protons. Catalytic currents between -1.2 to -2.4 mA cm^{-2} could be reached at -0.65 V vs. RHE , with **1a** showing the highest current densities (Fig. 2A and Table 2).

2.2.2. Heterogeneous electrochemistry. Taking advantage of the pyrene anchoring groups, the metallopolymer **1a–c** and complex **2** were then immobilized at the surface of MWNT modified electrodes (**1a–c**/MWNT and **2**/MWNT) following previously reported protocols.^{37,44} The loading of electrochemically active $[\text{2Fe2S}]^{\text{adt}}$ centers at the MWNT electrodes was estimated using data from CV measurements of **1a–c**/MWNT in CH_3CN . **1a–c**/MWNT showed a quasi-reversible reduction event at $E_{1/2} \approx -1.53$ to $-1.57\text{ V vs. Fc}^{+/0}$ ($\Delta E_{\text{p}} = 40\text{--}60\text{ mV}$) similar to that under homogeneous condition, again attributed to a one-electron redox process (*i.e.*, $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{I}}\text{Fe}^0$). The peak current of the latter process was found to vary linearly with scan rate, confirming the grafting of the catalysts (Fig. S21–S23 and Table S3†).⁵¹ Similarly, complex **2** showed a quasi-reversible signal at $\approx -1.63\text{ V vs. Fc}^{+/0}$ ($\Delta E_{\text{p}} = 35\text{ mV}$) (Fig. S24†). The relative cathodic shift of the redox potentials as compared to homogeneous (organic) conditions is attributed to the difference in employed solvent (DMF *vs.* CH_3CN).³⁷ A scan rate dependency study was difficult to perform for **2**/MWNT as the catalyst was leaching during CV in organic solvent, where the catalyst is soluble. Integration of the reduction wave allowed to estimate active site loadings of 3.7 ± 0.3 , 2.7 ± 0.4 , 2.3 ± 0.4 and $13.9 \pm 0.6\text{ nmol cm}^{-2}$ for **1a**, **1b**, **1c** and **2**, respectively (Table 2). We note that the observed loading is close to previously reported surface concentrations of electrochemically active metallopolymer of comparable composition and size (Table 2).⁴⁴ A complementary estimation of the active site loading was accomplished using ICP-OES which detected diiron active site surface concentrations of 6.80 ± 0.03 , 5.4 ± 0.1 , 3.8 ± 0.1 and $33.6 \pm 5.5\text{ nmol cm}^{-2}$ on MWNT for **1a**, **1b**, **1c** and **2** respectively (Table S4†). Comparing the active site density on electrodes estimated by CV and ICP-OES indicates that only 40–60% of the active sites present on the electrodes could be detected using CV for **1a–c** and **2**/MWNT. The lower loading value measured *via* CV may be explained by the specific behavior of surface-immobilized molecular species depending on their positioning with regards to the electrochemical double layer, as recently highlighted.⁵² As the synthesized polymers showcase a rather large size dispersity, it is likely that the environment varies slightly from one catalytic site to another, triggering an inhomogeneous redox response. In addition, this could also be linked to their positioning in the porous MWNT film as it is



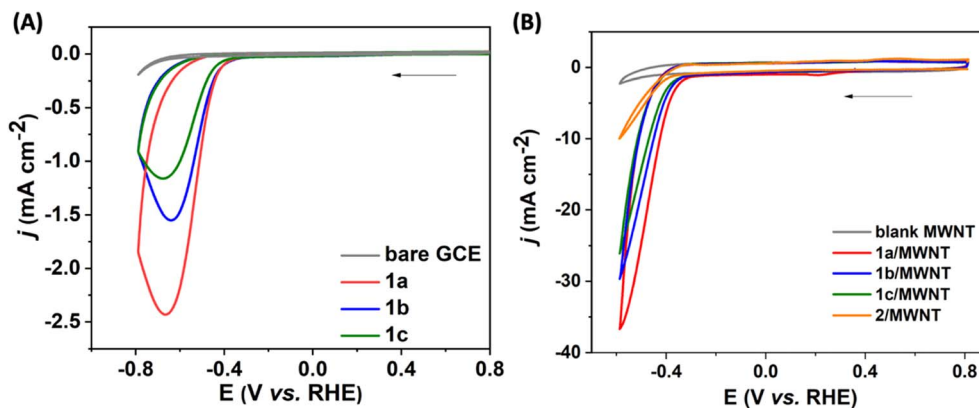


Fig. 2 CV of metallopolymers **1a–c** and complex **2**. (A) Homogeneous conditions with a concentration of 20 μM of **1a–c** at a GCE; (B) heterogeneous condition; following immobilization on MWNT/GCE. The CV measurements were compensated for ohmic drop (85%), in 0.2 M sodium phosphate buffer, pH 7 under argon ($\nu = 100 \text{ mV s}^{-1}$).

likely that deeply embedded metallopolymers have less access to electrolyte, thus directly impeding their redox response.^{53,54} Depending on the interplay between the electrolyte and the metallopolymers, this may result in variations in electrochemical activity and cause poor to silent response in CV experiments.⁵² Taken together these data indicate that a variety of active sites are present on our electrodes, including a fraction which is not directly detectable by CV.

The electrocatalytic properties of the modified electrodes were then characterized in 0.2 M phosphate buffer at pH 7. From CV measurements, the **1a–c**/MWNT modified electrodes displayed an onset potential ranging from -0.32 V to -0.33 V vs. RHE , and reached high current densities ranging from -24 ± 2 to $36 \pm 1 \text{ mA cm}^{-2}$ at -0.6 V vs. RHE . As observed in homogeneous conditions, the highest currents densities were observed with **1a** followed by **1b** and **1c** (Fig. 2B and Table 2). This can be rationalized by a higher surface loading of electrochemically active diiron catalyst. Importantly, switching from homogeneous to heterogeneous electrocatalysis with the metallopolymer, resulted in a significant drop in overpotential requirement and increase in catalytic current (Table 2). This is expected as diffusion limitations of the catalyst are circumvented following the immobilization of the metallopolymer at

the electrode,⁴⁴ and could also indicate improved electronic communication between the electrode surface and a large fraction of the catalytic sites. In contrast, the **2**/MWNT composite exhibited a notable cathodic shift in the onset potential of approximately 40–50 mV (*i.e.*, -0.37 V vs. RHE), along with a significantly lower current density of $-8 \pm 2 \text{ mA cm}^{-2}$ at -0.6 V vs. RHE compared to the metallopolymers under equivalent conditions. The substantial enhancement in the activity of the metallopolymers, despite a lower loading of active sites by 5–8 times compared to that of complex **2** (as per loading from ICP-OES), emphasizes the crucial role of the outer coordination sphere provided by the polymeric scaffold (Fig. 2B, orange trace, Table 2).⁴⁴

2.2.3. Bulk electrolysis coupled with gas chromatography.

In order to characterize the stability of the metallopolymer-functionalized electrodes under catalytic conditions and to quantify the amount of H_2 produced over time, chronoamperometry measurements (CA) were performed with the **1a–c**/MWNT modified electrodes. The CA experiments were carried out in neutral aqueous media (0.2 M phosphate buffer, pH 7) and the applied potential was set to -0.49 V vs. RHE for 20 hours. In parallel, the produced H_2 gas was detected and quantified by connecting the working electrode compartment of

Table 2 Quantitative analysis of the CV data of metallopolymers collected under homogeneous and heterogeneous conditions shown in Fig. 2. All CVs were performed in 0.2 M phosphate buffer at pH 7. The standard deviations were calculated based on a minimum of three independent experiments

Metallo polymer	Homogeneous condition		Heterogeneous condition		
	Onset potential ^a (V vs. RHE)	Current density at -0.65 V vs. RHE ^b (mA cm^{-2})	Onset potential ^a (V vs. RHE)	Current density at -0.6 V vs. RHE (mA cm^{-2})	Loading as per electrochemistry (nmol cm^{-2})
1a	-0.34	-2.42	-0.32	-36 ± 1	3.7 ± 0.3
1b	-0.35	-1.55	-0.33	-28 ± 1	2.7 ± 0.4
1c	-0.36	-1.17	-0.33	-24 ± 2	2.3 ± 0.4
2	nd ^c	nd	-0.37	-8 ± 2	13.9 ± 0.6

^a The onset potential is calculated as a potential where catalytic current deviates $\sim 10\%$ from the capacitive current of respective traces. ^b The standard deviations for homogeneous condition were marginal. ^c nd = not determined.



the electrochemical cell to an inline gas chromatography system (micro-GC).

At the beginning of the CA experiment, **1a**/MWNT showed an initial current density of $-2.7 \pm 0.2 \text{ mA cm}^{-2}$ (at $t = 1 \text{ min}$ to minimize capacitive current contribution). The current density was found to decline to $-0.3 \pm 0.1 \text{ mA cm}^{-2}$ during the initial six hours and then remained fairly stable, however quite close to the current obtained for bare MWNT (-0.17 mA cm^{-2}). This corresponds to retention of only $8 \pm 1\%$ of the initial current density (Fig. 3A, red trace, Table S5†). Increasing the pyrene content of the metallopolymer to $\sim 2.3 \text{ mol}\%$, resulted in a significant improvement in stability of the catalytic current. **1b**/MWNT showed an initial current density of $-2.8 \pm 0.1 \text{ mA cm}^{-2}$, comparable to **1a**/MWNT, which dropped to $-0.66 \pm 0.12 \text{ mA cm}^{-2}$ during the initial three hours. Following this initial current loss, the current density remained stable and $24 \pm 2\%$ of the initial current density was retained after 20 hours of electrolysis ($-0.65 \pm 0.10 \text{ mA cm}^{-2}$). Further increase in pyrene content, up to $6.6 \text{ mol}\%$ (**1c**/MWNT) caused a substantial drop in initial activity to $-0.9 \pm 0.1 \text{ mA cm}^{-2}$ (Fig. 3A, blue trace, Table S5†). The electrocatalytic activity of **1c**/MWNT then followed a similar trend to **1b**/MWNT with a steady decrease of current during the three first hours to then stabilize around $-0.35 \pm 0.08 \text{ mA cm}^{-2}$. Interestingly, this current could be retained for at least 20 hours, corresponding to $38 \pm 13\%$ of the initial current density (Fig. 3A, green trace, Table S5†). Thus, following an initial current loss during the first three hours, the current density was remarkably stable for **1b** and **1c**. Indeed, in the case of **1b** and **1c** about 90–95% of the current densities observed after three hours, were retained after 20 hours. This represents a substantial improvement from the recently studied metallopolymer by our group where stable catalytic activity could not be reached within 20 hours of CA.⁴⁴ CA of the **2**/MWNT exhibited an initial current density of $-0.9 \pm 0.1 \text{ mA cm}^{-2}$ (at $t = 1 \text{ min}$), gradually decreasing to $-0.20 \pm 0.01 \text{ mA cm}^{-2}$ (very close to blank *i.e.* -0.17 mA cm^{-2}). Overall, retention of $22 \pm 4\%$ of the initial current density was noted after 20

hours of CA (Fig. 3A, orange trace, Table S5†). The Faradaic efficiencies were estimated between 98–100% for all **1a–c**, **2**/MWNT based electrodes. As a result, 30 ± 1 , 54 ± 1 , 35 ± 2 and $16 \pm 1 \mu\text{mol}$ of H_2 corresponding to TON_{H_2} of $1.3 \pm 0.1 \times 10^4$, $3.8 \pm 0.3 \times 10^4$, $3.0 \pm 0.4 \times 10^4$ and $0.6 \pm 0.1 \times 10^3$ were estimated for **1a**, **1b**, **1c** and **2** respectively, after 20 hours of electrolysis (Fig. 3B, S25, Tables S5 and S6†). The corresponding turnover frequency (TOF_{H_2}) values, determined after the first hour of CA (reached the maximum value), were 0.8 ± 0.4 , 0.95 ± 0.20 and 0.8 ± 0.2 for **1a**, **1b** and **1c**, respectively. In contrast, complex **2** reached a maximum TOF_{H_2} of $0.008 \pm 0.001 \text{ s}^{-1}$, almost two orders lower than metallopolymer during CA. The TOF_{H_2} of the metallopolymer on longer time-scales can be found in the ESI† (Fig. S30 and Table S6†). It should be noted that the values of TON_{H_2} and TOF_{H_2} were estimated considering the total diiron active sites detected as per ICP-OES measurements and are thus most likely conservative.

In order to understand the loss of current, a *post-operando* analysis using CV, UV-vis and ICP-OES was performed on the catalysts-functionalized electrodes (Fig. S31–S33†). UV-vis spectra, collected for all catalysts following desorption from the MWNT film, showed negligible loss of pyrene after the electrolysis (Fig. S31†).^{37,44} This observation again underscores the strength of pyrene as an anchoring group on MWNT, as observed before for related diiron complex³⁷ and closely related metallopolymer.⁴⁴ Conversely, CV traces recorded in aqueous media after 20 hours of electrolysis revealed 70–90% loss and almost complete loss of the catalytic current (at -0.49 V vs. RHE) for **1a–c**/MWNT and **2**/MWNT, respectively (Fig. S32†). ICP-OES measurements of the iron content evolution of **1b**/MWNT at different time points of the CA showed a continuous loss of the iron concentration on the electrode *i.e.*, $\sim 12\%$, $\sim 40\%$, $\sim 70\%$ loss compared with the initial concentration after 1, 3 and 20 hours of CA, respectively (Table S6†). Thus, the long-term stability of the **1a–c**/MWNT metallopolymer can be rationalized by the relatively high retention of Fe during extended electrolysis. Indeed, the apparent stability of the active

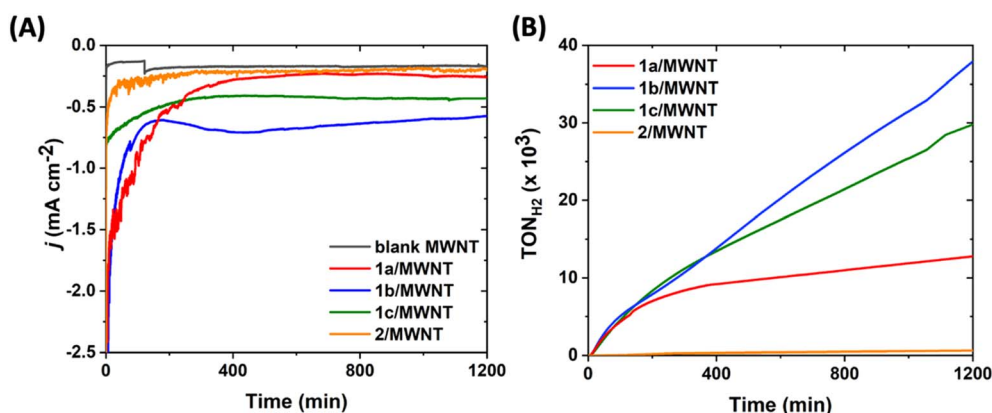


Fig. 3 CA of metallopolymer **1a–c** and complex **2** immobilized on MWNT/GCE. (A) Current density (j) vs. time; (B) turnover number (TON_{H_2}) vs. time recorded during CA at -0.49 V vs. RHE in 0.2 M sodium phosphate buffer, pH 7 under continuous flow of N_2 (5 mL min^{-1}). Here, bare MWNT, **1a**/MWNT, **1b**/MWNT, **1c**/MWNT and **2**/MWNT are represented by grey, red, blue, green and orange colors, respectively. The TON_{H_2} were calculated using loading from ICP-OES assessment.



sites is significantly improved in **1a-c**/MWNT when compared to the previously reported quinone-based [2Fe2S]-P(DMAEMA-*r*-PyBMA) (PyBMA = 4-(pyren-1-yl)-butyl methacrylate) metallopolymer.⁴⁴ Still, we note that the loss of current density of **1b**/MWNT only correlates weakly with the loss of Fe (Fig. S33 and Table S7†). The non-linear correlation between retained active sites (Fe ions) and activity again suggests the presence of different catalyst populations showcasing slightly different activities, where a relatively small fraction of highly active catalytic sites is lost relatively rapidly while slower but more robust catalysts remain active for several hours of electrolysis. The latter likely corresponds to a population of catalyst more deeply confined within the porous MWNT network or the polymer matrix bearing the active centre(s). The stable catalytic current are observed after three hours of CA could be attributed to the presence of (a) relatively stable population(s) of active sites that are not detected using CV measurement. Transformation of the CV-detectable [2Fe2S]^{adt} active sites to yield this second population of the active sites or to degraded products like metallic Fe, on an hour time-scale is unlikely to fully rationalize the observed currents, since **1a**/MWNT displays the highest initial Fe content but the lowest long term currents.

3. Conclusion

This study demonstrated that the {Fe₂(μ-adt)(CO)₆} derivatives can be incorporated within synthetic macromolecular scaffolds using free radical polymerization to prepare original metallopolymer, or “synthetic hydrogenases” (**1a-c**) with {Fe₂(μ-adt)(CO)₆} as active site. All studied metallopolymer were active for H₂ production at neutral pH both under homogeneous and heterogeneous conditions. The long-term stability and H₂ production activity of the surface immobilized metallopolymer were found to correlate with pyrene content, with the best performing metallopolymer, **1b** (~2.3 mol% of pyrene), which could reach a TON_{H₂} of 3.8 ± 0.3 × 10⁴ (estimated from loading as per ICP-OES) within 20 hours of CA at neutral pH, with a Faradaic efficiency close to unity. Increasing the pyrene content further, as in **1c** (~6.6 mol% of pyrene), improved the durability but at the expense of current densities relative to **1b**. The drop in activity with increasing amount of pyrene from could not be solely attributed to the catalyst loading. This is in good agreement with the notion that pyrene, albeit important for stability, also introduces hydrophobicity to the metallopolymer which decreases H⁺ diffusion to the catalytic sites.⁴⁴ Furthermore, the comparison of the activity of the metallopolymer to that of an isolated diiron site (complex **2**) allowed to confirm that the polymeric scaffold plays a crucial role in the catalytic process, enabling to reach TON values of about two orders of magnitude higher.⁴² This allows to decipher the role of each amine of the adt²⁻ and DMAEMA amine, where adt²⁻ is unlikely to act as a direct proton-shuttle to the Fe ions during hydride formation. In the case of the metallopolymer studied here, any protonation must occur after the injection of at least one-electron into the system, as evident from the titration of **1b**.

Electrochemical experiments of the metallopolymer hinted towards the presence of at least two populations of active sites

that likely differ *via* the nature of their electrostatic coupling with the electrode surfaces, arguably due to their various degree of confinement within the polymer matrix or the MWNT film. All metallopolymer display a rapid decrease of current density during the first hours, likely due to degradation of a more bulk exposed CV-detectable [2Fe2S]^{adt} active site population. Still, for **1b** and **1c** the current density remains stable from three hours until the end of the CA experiment. This observation along with the ICP-OES measurements suggest the existence of a variety of population of active sites with long-term stability and lesser activity within the porous MWNT electrodes.

In closing, additional efforts are clearly required to increase the stability of the catalytic units as well as their relative polymer content. In parallel, efforts need to be invested in increasing the surface loading and stability of the polymers on the electrode surface, as the observed currents are still in the low mA range. Finally, we note that the outlined synthesis strategy paves the way for functionalization with a broad range of (organometallic) active sites to support other relevant energy conversion reactions.

Conflicts of interest

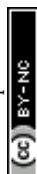
There are no conflicts to declare.

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