Introduction

In recent years, novel polymeric materials based on d-transition metal complexes, especially using ruthenium(II) and iridium(III) ions,1 gained special attention.2 In large area applications such as light-emitting devices,3 sensors4 and photosensitisers,5 new functional materials with tailor-made properties, good processing features and straightforward synthesis are of central importance. The covalent linkage of the complexes to a polymer leads to materials that have the advantage of preventing the aggregation of metal complexes as observed in polymer blends, while still maintaining the properties of the individual complexes. The properties of such materials can be effectively tuned by the choice of the metal ions, as well as by the chelating ligand.6,7

Recently, it was described that 2-(1H-1,2,3-triazol-4-yl)pyridine (triazole–pyridine) derivatives form highly photo-luminescent cyclometalated iridium complexes when used as ancillary ligands.8 The main advantage of using the triazole–pyridine-derived ligand is that the triazole moiety can be effectively synthesised and built into a variety of structures by using the highly efficient copper-catalysed azide–alkyne cycloaddition reaction (CuAAC),7 also referred to as the “click” reaction.9

Upon metal complexation, various structures with incorporated triazole–pyridine units can then allow for a versatile access to a new class of light-emitting materials.

In the literature, various examples of using the CuAAC reaction to combine different chromophores within one molecule10 or to attach multiple chromophores to a polymeric backbone11,12 are known; in all these examples, however, the triazole moiety has only been used as a covalent linker. Examples, where the triazole moiety would be employed as a functional linkage (e.g. serving also as a ligand13), are lacking.12 Thus, development of a modular approach to chromophoric iridium array materials, employing the triazole–pyridine moiety as a functional building block, was of interest. For this purpose, novel monomeric repeat unit 1 was designed and synthesised.

Monomer 1 possesses one triazole–pyridine unit that can coordinate to iridium(III) and is equipped with one azide and one acetylene group at each end. Polymerisation of an iridium-derived monomer 1 under the CuAAC conditions can afford polymer 2, a new type of chromophoric material equipped with phosphorescent iridium complexes along the heteroaromatic backbone.

The photophysical properties of such iridium-derived material are of interest since the properties can vary depending on the structure and can be readily tuned by modifying either the cyclometalating ligand (C–N) or the backbone. Furthermore, it was investigated whether the resulting photophysical properties of 2 are similar to those of the individual iridium centres or whether there is a significant electron or energy transport (through space or through the backbone) between the iridium centres. An earlier study of photophysical properties of polymers with alternating triazole and fluorene units revealed that there

Triazole–pyridine ligands: a novel approach to chromophoric iridium arrays†

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We describe a novel modular approach to a series of luminescent iridium complexes bearing triazole–pyridine-derived ligands that were conveniently prepared by using “click” chemistry. One, two or three triazole–pyridine units were effectively built into the heteroaromatic macromolecule using versatile acetylene- and azide-functionalised precursors. Using this approach, a series of iridium-derivated molecules, that differ in the number of iridium centres, the structural characteristics of the cyclometalating ligand and the backbone, were synthesised. The preliminary photophysical properties of the prepared complexes indicate that there is only limited interaction (through space or through the backbone) between the iridium centres within one molecule and that each iridium centre retains its individual properties. The results show that our approach can be generally applied towards covalently linked multichromophoric systems with potential application, for instance, in the design and preparation of tunable light emitters. As a demonstration of this concept, a single molecule white-light emitter, constructed from two iridium centres (yellow emission) and a fluorene unit (blue emission), is presented.
was only poor electron or energy transport between the fluorene units which retained their individual properties. These results indicated that conjugation is not extended through the formally sp\(^{3}\) hybridised nitrogen atom (1-N) of 1,2,3-triazole group, even though according to extensive molecular modelling, the triazole moiety is known to be flat. As a consequence, the CuAAC approach represents an efficient tool to access novel versatile chromophoric building blocks and to combine various chromophoric units via covalent linkages.

In this report, we describe a modular synthetic approach to multichromophoric triazole–pyridine-derived oligomers using the CuAAC reaction. Preliminary photophysical studies indicate that in the prepared molecules, the individual chromophoric components retain their luminescent properties. Consequently, the overall emission spectrum of the ensemble can readily be tailored.

**Results and discussion**

**Molecular design**

Initial attempts to synthesise Ir(ppy)\(_2\)(I) by reacting I with (ppy)\(_2\)(μ-Cl)Ir(ppy)\(_2\) resulted in fast decomposition of the azide group probably initiated by light and/or heat. An alternative approach, where I would first undergo polymerisation using the CuAAC reaction and subsequent reaction with (ppy)\(_2\)(μ-Cl)Ir(ppy)\(_2\) to afford 2, proved also not to be satisfactory; only short oligomers of I were formed and their poor solubility inhibited further growth of the polymeric chain. To overcome these problems, two types of oligomeric compounds containing one or more triazole–pyridine units were designed and synthesised, and are schematically represented in Fig. 1, and summarised in Tables 1 and 2. In these structures, no azide groups are present; thus, the corresponding iridium complexes could be isolated and purified, allowing a systematic study of their photophysical properties.

In the Type A system (Table 1), two triazole–pyridine moieties and their corresponding Ir(C=\(N\))\(_2\) complexes were connected through a series of heteroaromatic spacers. The spacers differed in length (3 and 4), electronic properties (4, 5 and 6) and substitution of the central benzene ring (para versus meta; 4 and 7). Towards making oligomers/polymers (Type B), an alternative strategy was required (Table 2); the oligomers were grown stepwise from one end, which resulted in a parallel orientation of the repeat unit in contrast to the antiparallel orientation in Type A (Fig. 1). In this system, oligomers of different length (8–12) were synthesised and in one case, the conjugation was interrupted by the insertion of a cyclohexane-1,4-diyl unit into the heteroaromatic backbone (12).

To prepare the triazole–pyridine-based ligands in a modular and efficient manner by using the CuAAC reaction, precursors 13 and 14 were designed and synthesised as versatile monomeric building blocks. The antiparallel dimeric (3a–6a) and trimeric (7a) ligands were effectively synthesised by using 13 and the spacers 15, 16, 14, 17 and 18. The parallel oligomeric ligands 8a–10a and 12a were prepared starting from the acetylene-functionalised blocking group 19 by the stepwise growth of the oligomeric chain using 13 and 14, respectively (Fig. 2).

**Table 1 Structures of the prepared “antiparallel” dimeric/trimeric oligomers (Type A)**

<table>
<thead>
<tr>
<th>Dimer</th>
<th>Spacer</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a–3c</td>
<td><img src="image" alt="Spacer 3a–3c" /></td>
</tr>
<tr>
<td>4a–4c</td>
<td><img src="image" alt="Spacer 4a–4c" /></td>
</tr>
<tr>
<td>5a–5c</td>
<td><img src="image" alt="Spacer 5a–5c" /></td>
</tr>
<tr>
<td>6a–6c</td>
<td><img src="image" alt="Spacer 6a–6c" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trimer</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td><img src="image" alt="Trimer 7a" /></td>
</tr>
<tr>
<td>7b</td>
<td><img src="image" alt="Trimer 7b" /></td>
</tr>
</tbody>
</table>

Fig. 1 Schematic representation of the prepared oligomers with antiparallel (Type A) and parallel (Type B) orientation of the triazole–pyridine units (BG = blocking group).
The monomeric building blocks 13 and 14 were synthesised in four steps starting from commercially available 2,5-dibromo-pyridine (20) via the key intermediate 22 (Scheme 1). Compound 22 was equipped in the 2 and 5 positions with two differently protected acetylene groups (TMS and TIPS, respectively) that were attached in two steps starting from 20 by a series of Sonogashira cross-coupling reactions. In the first step, the substitution reaction took place exclusively in the 2 position, affording the intermediate 21, due to the increased polarity of the C–Br bond in the 2 position compared to 5. Despite the increased reactivity of pyridine electrophiles in cross-coupling reactions (compared to benzene), high selectivity was achieved by carrying out the reaction under the mild conditions (room temperature).

Selective deprotection of TMSA group in 22 provided the intermediate 23 that after the reaction with an excess of diazides 24 and 25 under the standard conditions (CuI, PMDTA) afforded the desired monomeric building blocks 13 and 14, respectively.

The acetylene-functionalised blocking group 19 was efficiently synthesised starting from 1,3,5-tribromobenzene (26) via the triacetylene-derived intermediate 28 (Scheme 2). Similarly to 22, compound 28 was also obtained by a series of Sonogashira cross-coupling reactions via the intermediate 27. The moderate selectivity of the first step led to the formation of the mono- and trisubstituted side products. The propane-2-ol moiety was chosen as a protecting group to enable easy separation of 27 by column chromatography. Selective deprotection reaction of the acetylene groups protected by propane-2-ol moiety in 28 afforded the precursor 29. Subsequent reaction of 29 with two equivalents of bulky azide 30 provided 31. The desired blocking group 19 was obtained after the deprotection reaction of 31 using TBAF in 90% yield.
The dimeric ligands 4a-6a were prepared by reacting two equivalents of 13 with one equivalent of the corresponding diacetylene spacer (15–17) under the standard conditions (CuI, PMDTA); for the trimeric ligand 7a, the reaction was done with three equivalents of 13 and the triacetylene-derived spacer 18. In order to minimise the length of the spacer, 3a was synthesised using the intermediate 23 as a monomeric building block and the diazide 24 as a spacer. In all cases, the desired ligands were obtained in good to excellent yields (Table 3).

The oligomeric ligands 8a–10a and 12a were prepared starting from the acetylene-functionalised blocking group 19 and the monomeric building blocks 13 and 14 by using the stepwise clicking/deprotection process, as shown in Scheme 3. By incorporating the blocking group, the oligomeric chain could easily be extended in the two-step unidirectional process for an extra monomeric unit. At the same time, the bulky substituents of 19 prevented the aggregation of the prolonged chain and retained the solubility. As such, this approach represents an elegant and modular way to well-defined unidirectional oligomeric triazole–pyridine-derived macromolecular structures.

Two series of the target chromophoric molecules b (3b–8b and 10b) and c (3c–6c and 8c–12c) were effectively obtained starting from the synthesised ligands 3a–10a and 12a. Heating of the mixture of the ligand and a slight excess of [Ir(C$_3$N)$_2$Cl$_2$] (corresponding C–N ligands are depicted in Tables 1 and 2) afforded the corresponding iridium compound in good to excellent yield. Usually, heating to 50 °C for two hours was sufficient to achieve a complete conversion; in the case of 4b, a prolonged reaction time was necessary due to the restricted solubility of 4a. All target compounds exhibited good solubility in CH$_2$Cl$_2$ and CHCl$_3$, and gradient column chromatography using CHCl$_3$/MeOH as an eluent proved to be very efficient as a purification technique. ESI-MS analysis of the pure products did not show the presence of mono(ridium) species in the case of the dimers; similarly, no mono- and bis(ridium) species were detected in the case of the trimer. Additionally, all binuclear iridium complexes were obtained as a 1:1 mixture of two diastereomers (for more information, see the ESI†).

### Photophysical properties

Target molecules 3b–8b, 10b, 3c–6c, 8c and 10c–12c were investigated by the preliminary photophysical and electrochemical studies; the photophysical results are summarised in Table 4. In terms of the cyclometalating ligands coordinated to iridium (see Tables 1 and 2), the target compounds can be divided into two classes (b and c series). Triazole–pyridine-derived iridium complexes analogous to the complexes in the b series were previously described and their ligand centred (1LC) excited states were found to be localised primarily on the cyclometalating ligand. Triazole–pyridine-derived iridium complexes analogous to the complexes in the c series have not been described before; by comparing similar examples from the literature, 3LC excited states are, however, expected to be localised on the triazole–pyridine ligand. In terms of the triazole–pyridine ligand (see Tables 1 and 2), each series can be further divided into two subclasses (“antiparallel” type A and “parallel” type B, see Fig. 1).

All target molecules show emission in the green to yellow part of the spectrum at room temperature except for compound 6c, which shows additional emission in the blue part of the spectrum. The luminescence quantum yields of the complexes measured in air equilibrated conditions were lower when compared to those in argon saturated conditions. This is due to the triplet nature of the emissive state of the iridium complex that is easily quenched by the ground state oxygen present in solution. It can be seen that in air equilibrated conditions, the quantum yields are all very similar (0.01–0.04) except for compound 6c, which was observed to have a significantly lower quantum yield (ca. factor 10). Similar values of measured quantum yields of our compounds are in agreement with previous observations; in a series of complexes with two ppy cyclometalating ligands and a third highly conjugated phenylethynyl ligand a reasonably constant quantum yield along a similar but rather short series of complexes was observed. This interesting effect has been ultimately associated to the high spin–orbit coupling of the iridium centre (heavy atom effect). In argon saturated conditions, compounds 8b and 10c have a small increase in the value of their luminescence quantum yield by a factor between 6 and 9; in all other cases, the compounds have an increase in their quantum yields by a similar factor, between 1 and 5.

From the steady state measurements at room temperature, clearly two groups arise (Fig. 3, Table 4). One group of complexes (4b, 10b, 10c, 11c and 12c) has a relative blue shift in their emission that shows a more structured emission profile characteristic of 3LC emission and one highest maximum of 507 and 518 nm (towards green colour). The second group (3b, 5b–8b, 3c–6c and 8c) has a much broader emission profile and a relative red shift in the emission with the maximum of emission between 539 and 553 nm (towards yellow colour). The former emission profile can be ascribed to an emissive state closer in character to the 3LC excited state whereas the latter can be ascribed to have a stronger 3MLCT character. A similar example was described previously in the literature; compounds that shared the same iridium emissive core Ir(ppy)$_2$L

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**Table 3** Summary of the precursors and the isolated yields for the “antiparallel” dimeric and trimeric ligands 3a–7a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomeric building block</th>
<th>Spacer</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>24</td>
<td>3a</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>15</td>
<td>4a</td>
<td>98$^a$</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>16</td>
<td>5a</td>
<td>47</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>17</td>
<td>6a</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>18</td>
<td>7a</td>
<td>51$^a$</td>
</tr>
</tbody>
</table>

$^a$ Yield of the crude product; purification was inhibited by the restricted solubility of 4a. $^b$ Purity not determined due to the aggregation of 7a.

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**Scheme 3** Synthesis of the “parallel” oligomeric ligands 8a, 10a and 12a.
were found to have a more 3LC or 3MLCT emissive state depending on the variations introduced in the third ligand L.\textsuperscript{16,18} In the low temperature and rigid matrix conditions, the corresponding blue shifts are observed for all complexes and the emission profiles become clearly resolved, showing the vibronic structure of the emissive state and indicating a 3LC emission.

Most of the measured lifetimes at room temperature are clearly biexponential indicating the decay of more than one excited state at the same time. These could result from the different excited states within the same complex (3LC or 3MLCT) or different isomers (all binuclear complexes were obtained as a 1 : 1 mixture of two diasteromers; for more information, see the ESI\textsuperscript{†}) or a combination of these factors. In air equilibrated conditions, the lifetimes span from 0.10 to 2.3 ms and they become significantly longer in argon saturated conditions due to the triplet character of the emitting states. At low temperature (77 K) in rigid matrix conditions, the general tendency observed is a very slow biexponential decay composed of one component with a lifetime of around 4 ms and one very long component of up to 24 ms. The components in the range of a few ms are characteristic for 3MLCT (\( \tau \approx 5 \) ms) emissive states while the much longer components are ascribed to 3LC emissive states.\textsuperscript{19}

In general, the described photophysical properties of the target molecules are not significantly altered by changes within the structure. When a more detailed comparison of the structures of the prepared molecules is carried out, two groups with general structural difference can be recognised. In one group, the heteroaromatic backbone possesses only one (8b and 8c), two (3b–6b and 3c–6c) or three (7b) triazole–pyridine moieties, each bearing an acetylene group in the 5 position of the pyridine unit. In the second group, one triazole–pyridine moiety bears a triazole group instead of an acetylene group in the 5 position of the pyridine unit (10b, 10c, 11c and 12c).

![Table 4 Photophysical characterisation data of the studied iridium complexes\textsuperscript{a}](image)

- \( \Phi_{\text{air}} \): Fluorescence quantum yield in air.
- \( \Phi_{\text{argon}} \): Fluorescence quantum yield in argon.
- \( \tau_{\text{air}} \): Lifetime in air.
- \( \tau_{\text{argon}} \): Lifetime in argon.

For a more detailed photophysical characterisation, see the ESI\textsuperscript{†}.

Excitation at 355 nm. Measured in THF/CH\(_2\text{Cl}_2\) (9 : 1). These compounds showed a very high scattering in the rigid matrix that did not allow a good statistical analysis of the time resolved data.

![Fig. 3 Characteristic examples of the emission spectra at room temperature (excitation at 355 nm) of the prepared complexes with a relative red (8c) and a relative blue shift (10c–12c) obtained from the steady state measurements.](image)
Previous studies indicate that conjugation cannot be significantly extended through the sp³ hybridised nitrogen of the triazole; it can, however, be extended through the 5 position of the pyridine unit. Considering this, one iridium atom of 10b, 10c, 11c and 12c is coordinated to the ancillary triazole–pyridine ligand with conjugation extended for an extra triazole group (it should be noted that the triazole moiety is more electron deficient than the acetylene group). Except for 4b, molecules of these groups correlate with the molecules of the two groups obtained from the steady state measurements. These results indicate that the blue shift in the emission of 10b, 10c, 11c and 12c can be associated with the described extended conjugation effect (Fig. 3). Interruption of the conjugation by the sp³ hybridised nitrogen of the triazole is further supported; no effect on the emission spectra of the dimeric/trimeric molecules that differ in the spacer length (3 and 4), electronic properties (4–6) and substitution of the central benzene ring (4 and 7) was observed. These conclusions are in agreement with previous observations in the literature and show that using this approach, a number of chromophores can be effectively linked together maintaining their individual properties. Such an approach is suitable for the preparation of oligomeric/polymeric d⁰ transition metal complexes with potential applications in light-emitting devices.

Covalent linking of various chromophores within one structure has recently gained special interest, especially for applications in design and preparation of white-light emitters. Here, we would like to demonstrate that our approach, employing the “click” reaction to construct chromophoric iridium array materials, represents an efficient tool also towards this goal. Compounds 6b and 6c are an example where one chromophoric fluorene unit equipped with two acetylene groups was covalently linked using the CuAAC reaction with two iridium chromophores. The photophysical properties of compound 6b are very similar to the properties of other compounds in the b series; the photophysical properties of compound 6c are, however, significantly different. As mentioned before, the values of the quantum yield and the lifetime of 6c are significantly lower (ca. by a factor 10) compared with other quantum yields (Table 4). Moreover, apart from the emission in the green to yellow part of the spectrum that is ascribed to the iridium chromophore, compound 6c shows emission in the blue part of the spectrum that is ascribed to thefluorene chromophore (Fig. 4).

The reason for such a dramatic decrease of the quantum yield in the case of 6c is not understood and will be a subject of future investigation. Nevertheless, the combination of the “blue” and “green to yellow” emission of 6c leads to the “white-like” emission observed by a naked eye, as depicted in Fig. 5. Our approach allows us to further tune the properties of the prepared complexes by postmodification of the peripheral acetylene groups. Moreover, a number of different chromophores can be readily combined and their ratio, that will provide the desired properties (e.g. “the perfect white”), can be effectively controlled.

Conclusions

In summary, this paper describes a novel modular synthesis of a series of triazole–pyridine-derived ligands and their luminescent iridium(III) complexes bearing two additional cyclometalating ligands using “click” chemistry, and the preliminary studies of their photophysical properties. One, two or three iridium centres were effectively linked through a series of heteroaromatic spacers using versatile acetylene- and azide-functionalised precursors in good to excellent overall yields. The photophysical properties of all target molecules are not significantly altered by changes within the structure (spacer properties, number of iridium centres and cyclometalating ligands) and indicate that the conjugation in the heteroaromatic backbone cannot be extended through the sp³ hybridised nitrogen atom of the triazole. Accordingly, very little interaction (through space or through the backbone) between the iridium centres within one molecule was observed, indicating that each iridium centre retains its individual properties.

Finally, our approach is of interest for design and construction of various light-emitting materials by covalent linking of different chromophores, including versatile tuning of the material properties, using “click” chemistry. One example of such an application was demonstrated; two iridium centres showing “yellow” emission and one fluorene unit showing “blue” emission.
were combined via the covalent linkage to provide a white-light emitter. Interestingly, when comparing two analogous compounds in the “white-emitter” series bearing 2-phenylpyridine or 2-\((1H\)-pyrazol-1-yl\)pyridine as cyclometalating ligands, white-light emission was only observed in the latter case. More detailed investigation of the photophysical properties of this new class of compounds and their applications in light-emitting materials, including energy transfer kinetics and electroluminescence studies in thin films, will be the subject of our future research.

**Experimental**

**Setups**

The photophysical measurements were carried out at Universiteit van Amsterdam. Electronic absorption spectra were recorded in a quartz cuvette (1 cm, Hellma) on a Hewlett-Packard 8543 diode array spectrometer (range 190–1100 nm). Steady state fluorescence spectra were recorded using a Fluorolog 3 (Spx 1681) fluorimeter equipped with a Xe arc light source, a Hamamatsu R928 photomultiplier tube detector and a double excitation and emission monochromator. Emission spectra were corrected for source intensity and detector response by standard correction curves, unless stated otherwise. Emission quantum yield were measured in optically dilute solutions, using the indicated reference solution, according to the following:

\[
\Phi_U = \frac{[\text{A}_U \text{I}_{U} \eta_{U}^2]}{[\text{A}_I \text{I}_{I} \eta_{I}^2]} \Phi_I
\]

where \(u\) and \(r\) are the unknown and the reference, respectively, \(\Phi\) is the luminescence quantum yield, \(A\) is the absorption factor at the excitation wavelength (<0.1), \(I\) is the integrated emission intensity and \(\eta\) is the refractive index of the solvents. Lifetimes of excited states were determined using a Nd:YAG master (7 ns pulses fwhm, excitation wavelength 355 nm) and a Hamamatsu C5680-21 streak camera equipped with Hamamatsu M5677 low speed single sweep unit. Streak cameras are high-speed light detectors, which enable detection of the fluorescence as a function of the spectral and the time evolution simultaneously.

**Samples**

The stock solutions were prepared by dissolving the sample in a minimum amount of CH\(_2\)Cl\(_2\) and then the CH\(_2\)Cl\(_2\) solution was diluted with THF (solvents Uvasol grade). All complexes showed a good solubility in CH\(_2\)Cl\(_2\) except for 4c. As a reference, Ru(bpy)\(_3\)Cl\(_2\) in water was used (\(\Phi_{\text{air}} = 0.028\) and \(\Phi_{\text{argon}} = 0.042\)).
All compounds showed a good stability as proven by no changes in their UV-Vis spectra before and after the measurements, except for compound 3c that showed the disappearance of a band centered at 315 nm probably due to photodecomposition. In several of the time resolved experiments at low temperature (77 K) in rigid matrix, a complete precipitation of the complexes was observed during the freezing procedure. These molecules showed limited solubility in the solvents that give good glassy matrices (butyronitrile, ethanol, etc.) making the time resolved measurement under these conditions rather difficult.

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**Notes and references**

It was, however, necessary to use slightly less than one equivalent of TMSA to avoid the formation of the disubstituted side product that could only be removed by preparative HPLC. Minor fractions of unreacted 20 (usually not more than 5%) were easily removed by crystallisation from MeOH/H\textsubscript{2}O mixture by the successive decrease of the MeOH/H\textsubscript{2}O ratio.

In addition to the photophysical characterisation, the electrochemical characterisation of the selected iridium complexes by using cyclic voltammetry was also carried out. For compound 3c, reversible oxidation at +1.01 V and irreversible reduction at −1.83 V were observed. For all other compounds, not reproducible oxidation and, in some cases, irreversible reduction at around −1.8 V were observed. For more information, see the ESI†.


