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

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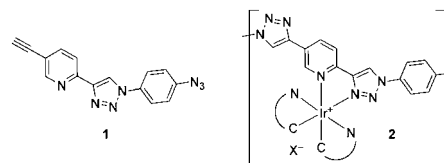
We describe a novel modular approach to a series of luminescent iridium complexes bearing triazole–pyridine-derived ligands that were conveniently prepared by using “click” chemistry. One, two or three triazole–pyridine units were effectively built into the heteroaromatic macromolecule using versatile acetylene- and azide-functionalised precursors. Using this approach, a series of iridium-derived 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.

Introduction

In recent years, novel polymeric materials based on d⁶ 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.^{1a}

Recently, it was described that 2-(1*H*-1,2,3-triazol-4-yl)pyridine (triazole–pyridine) derivatives form highly photoluminescent cyclometalated iridium complexes when used as ancillary ligands.⁶ 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.⁸ 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 molecule⁹ or to attach multiple chromophores to a polymeric backbone^{2c,2e,10} 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 ligand¹¹), 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

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† Electronic supplementary information (ESI) available: Synthesis and characterisation data for all compounds, and photophysical characterisation and emission profiles of all target molecules. See DOI: 10.1039/c0jm03117h

was only poor electron or energy transport between the fluorene units which retained their individual properties.¹³ 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 $\text{Ir}(\text{ppy})_2(\mathbf{1})$ by reacting $\mathbf{1}$ with $(\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{ppy})_2$ resulted in fast decomposition of the azide group probably initiated by light and/or heat. An alternative approach, where $\mathbf{1}$ would first undergo polymerisation using the CuAAC reaction and subsequent reaction with $(\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{ppy})_2$ to afford $\mathbf{2}$, proved also not to be satisfactory; only short oligomers of $\mathbf{1}$ 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 $\text{Ir}(\text{C}^*\text{N})_2$ 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

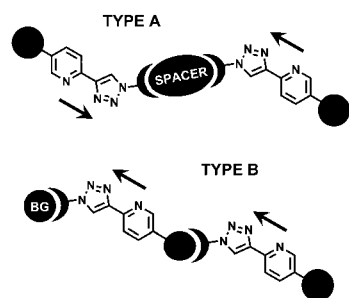


Fig. 1 Schematic representation of the prepared oligomers with antiparallel (Type A) and parallel (Type B) orientation of the triazole–pyridine units (BG = blocking group).

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

TYPE A (DIMER)	
a: No $[\text{Ir}(\text{C}^*\text{N})_2]^+$ b: $\text{C}^*\text{N} =$ c: $\text{C}^*\text{N} =$	
Dimer	Spacer
3a–3c	
4a–4c	
5a–5c	
6a–6c	
TYPE A (TRIMER)	
Trimer	R
7a	
7b	

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).

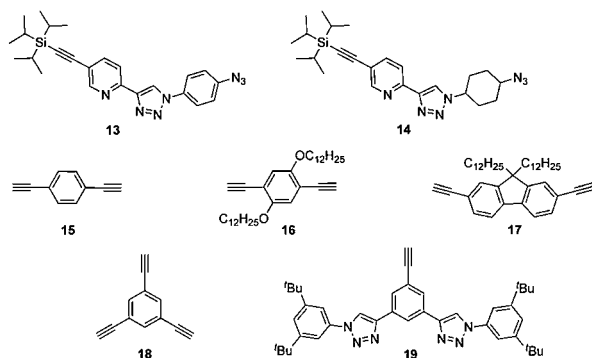
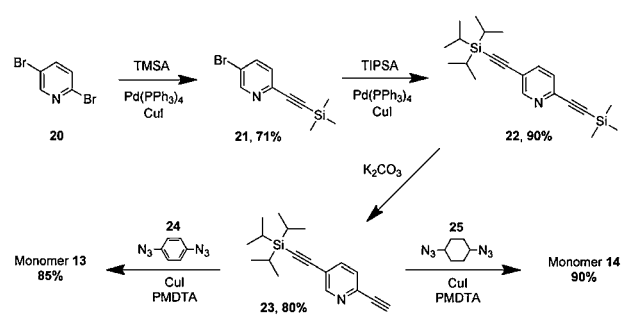
Table 2 Structures of the prepared “parallel” monomers and oligomers (Type B)

Cmpd	n	R
8a–8c	1	TIPSA ^a
9a, 9c	1	Ethynyl
10a–10c	2	TIPSA ^a
11c	1	
12a	1	
12c	1	

^a (Triisopropylsilyl)ethynyl.

Synthesis

The monomeric building blocks **13** and **14** were synthesised in four steps starting from commercially available 2,5-dibromopyridine (**20**) via the key intermediate **22** (Scheme 1). Compound **22** is 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

**Fig. 2** Structures of the monomeric building blocks **13** and **14**, the spacer molecules **15–18** and the blocking group **19**.**Scheme 1** Synthesis of the monomeric building blocks **13** and **14**.

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).¹⁵ 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.

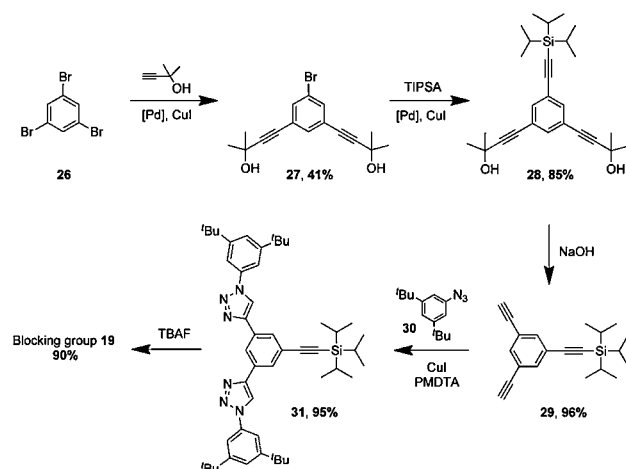
**Scheme 2** Synthesis of the blocking group **19**.

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

Entry	Monomeric building block	Spacer	Product	Yield (%)
1	23	24	3a	92
2	13	15	4a	98 ^a
3	13	16	5a	47
4	13	17	6a	88
5	13	18	7a	51 ^b

^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**.

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[∞]N)₂]₂Cl₂ (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 CH₂Cl₂ and CHCl₃, and gradient column chromatography using CHCl₃/MeOH as an eluent proved to be very efficient as a purification technique. ESIMS analysis of the pure products did not show the presence of mono(iridium) species in the case of the dimers; similarly, no mono- and bis(iridium) 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 electrochemical¹⁶ 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 (³LC) excited states were found to be localised primarily on the cyclometalating ligand.^{6b} 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,¹⁷ 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.* by 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.¹⁸ This interesting effect has been ultimately associated to the high spin-orbit coupling of the iridium centre (heavy atom effect).^{1b} 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 emission between 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)₂L

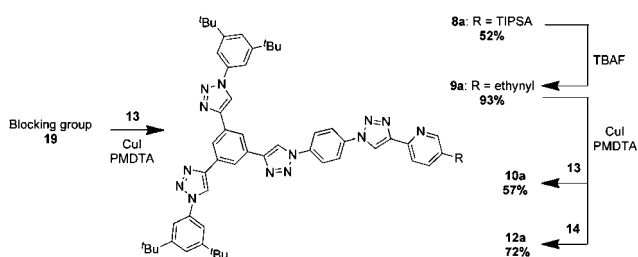
**Scheme 3** Synthesis of the “parallel” oligomeric ligands **8a**, **10a** and **12a**.

Table 4 Photophysical characterisation data of the studied iridium complexes^a

Cmpd	Emission at room temperature ^{bc}					Emission at 77 K ^b τ/μs
	λ _{max} /nm	Φ _{air}	Φ _{argon}	τ _{air} /μs	τ _{argon} /μs	
3b	551	0.01	0.05	0.16	0.20	4.1
4b	513	0.02	0.08	1.3 (18%) 0.34 (82%)	1.8 (25%) 0.78 (75%)	4.3
5b	553	0.03	0.14	1.53 (60%) 0.40 (40%)	2.10 (23%) 0.91 (77%)	^d
6b	546	0.01	0.03	2.1 (3%) 0.50 (97%)	8.0 (1%) 1.6 (99%)	^d
7b	543	0.03	0.08	1.82 (10%) 0.80 (90%)	1.78 (20%) 0.69 (80%)	^d
8b	550	0.03	0.19	0.14	0.21	4.4
10b	518	0.02	0.05	0.17 (17%) 0.04 (83%)	1.6 (61%) 0.31 (39%)	4.5 (25%) 1.7 (75%)
3c	539	0.02	0.05	0.43 (31%) 0.20 (69%)	0.31 (75%) 0.11 (11%)	15.0 (40%) 4.0 (60%)
4c	547	0.04	0.05	0.54 (12%) 0.20 (88%)	2.10 (24%) 0.86 (76%)	17.5 (22%) 5.43 (78%)
5c	540	0.01	0.04	0.54 (10%) 0.2 (90%)	0.69 (4%) 0.19 (90%)	^d
6c	544	0.001	0.005	0.34 (62%) 0.05 (38%)	2.00 (11%) 0.47 (89%)	^d
8c	540	0.02	0.08	0.58 (25%) 0.19 (75%)	0.56 (51%) 0.25 (49%)	17.0 (44%) 4.8 (56%)
10c	511	0.04	0.34	0.42 (74%) 0.10 (26%)	0.66 (30%) 0.18 (70%)	14.0 (30%) 3.3 (70%)
11c	507	0.01	0.03	0.5 (3%) 0.17 (97%)	1.0 (13%) 0.3 (87%)	24.0 (23%) 5.0 (77%)
12c	507	0.03	0.10	2.3 (39%) 0.7 (61%)	2.3 (15%) 0.84 (85%)	17.0 (50%) 4.5 (50%)

^a For a more detailed photophysical characterisation, see the ESI†. ^b Excitation at 355 nm. ^c Measured in THF/CH₂Cl₂ (9 : 1). ^d These compounds showed a very high scattering in the rigid matrix that did not allow a good statistical analysis of the time resolved data.

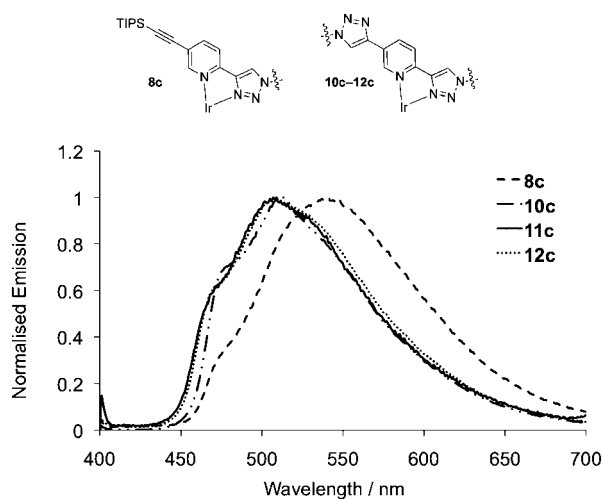


Fig. 3 Characteristic examples of the emission spectra at room temperature (excitation at 355 nm) of the prepared complexes with a relative red (**8c**) and a relative blue shift (**10c–12c**) obtained from the steady state measurements.

were found to have a more ³LC or ³MLCT emissive state depending on the variations introduced in the third ligand L.^{1b,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 diastereomers; for more information, see the ESI†) or a combination of these factors. In air equilibrated conditions, the lifetimes span from 0.10 to 2.3 μs 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 μs and one very long component of up to 24 μs. The components in the range of a few μs are characteristic for ³MLCT (τ ≈ 5 μs) emissive states while the much longer components are ascribed to ³LC emissive states.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**).

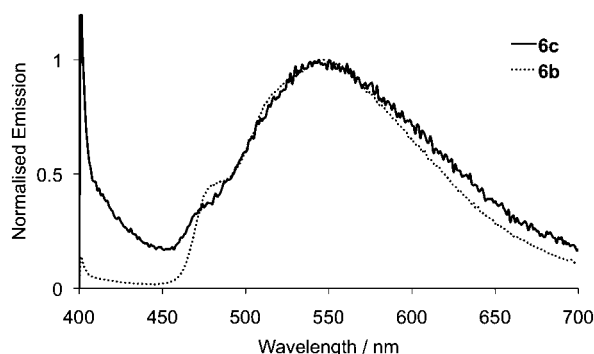


Fig. 4 Emission profiles at room temperature (excitation at 355 nm) of **6b** and **6c** containing two different chromophoric units. Compound **6c** shows emission in the blue (fluorene) and in the green to yellow (iridium) part of the spectrum resulting in the white-like emission.

Previous studies indicate that conjugation cannot be significantly extended through the sp^3 hybridised nitrogen of the triazole;¹³ 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 sp^3 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 literature¹³ and show that using this approach, a number of chromophores can be effectively linked together maintaining their individual

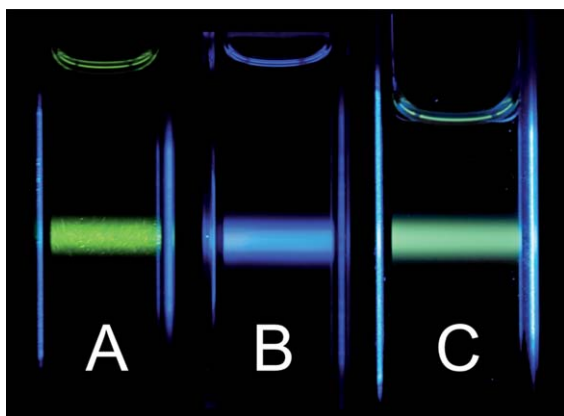


Fig. 5 “Green to yellow” emission of **4c** containing iridium chromophore (A), “blue” emission of **6a** containing fluorene chromophore (B) and “white-like” emission of **6c** containing both iridium and fluorene chromophores (C), as observed by a naked eye. Excitation at 333.6–363.8 nm (Spectra-Physics BeamLok 2085–15S Argon Laser with MidUV Multiline mirrors, 40 mW).

properties. Such an approach is suitable for the preparation of oligomeric/polymeric d^6 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.^{2a,20} 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 the fluorene 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”^{20a}), 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 sp^3 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-(1*H*-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 (Spex 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:

$$\Phi_u = [(A_r I_r n_u^2)/(A_u I_u n_r^2)]\Phi_r$$

where *u* and *r* are the unknown and the reference, respectively, Φ is the luminescence quantum yield, *A* is the absorption factor at the excitation wavelength (<0.1), *I* is the integrated emission intensity and *n* is the refractive index of the solvents. Lifetimes of excited states were determined using a Nd:YAG laser (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 CH₂Cl₂ and then the CH₂Cl₂ solution was diluted with THF (solvents Uvasol grade). All complexes showed a good solubility in CH₂Cl₂ except for **4c**. As a reference, Ru(bpy)₃Cl₂ in water was used ($\Phi_{\text{air}} = 0.028$ and $\Phi_{\text{argon}} = 0.042$).²¹ 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 centred 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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- 15 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/H₂O mixture by the successive decrease of the MeOH/H₂O ratio.
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