Functionalization of polymers with phosphorescent iridium complexes *via* click chemistry†

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We report a simple yet highly efficient route to prepare polymers with a variety of pendant iridium complexes as potential materials in organic light-emitting diodes by employing click chemistry.

Cyclometalated Ir(III) complexes have been studied extensively as active compounds in organic light-emitting diodes (OLEDs).[1] Efficient electrophosphorescence of these complexes arises from the intersystem crossing from the singlet to the triplet excited state, allowing such complexes to utilize both singlet and triplet excitons.[1,2] Therefore, 100% internal quantum efficiencies can be achieved for OLEDs based on iridium complexes.[2]

While iridium complexes in general are excellent candidates for optical devices, small molecule metal complexes are difficult to process. Such complexes have to be either vacuum deposited or doped into polymer matrices, often resulting in phase separation and poor device performance. A more appealing strategy is the covalent attachment of the desired metal complex to a polymer backbone. The resulting covalently functionalized polymers can be solution processed, thereby preventing phase separation and poor device performance.[3] We have previously employed this strategy to prepare solution processable materials with various complexes based on aluminium,[4,5] zinc,[4] ytterbium,[4] and iridium.[6,7]

In these reports, the functionalized polymers were synthesized either by the polymerization of monomers containing the desired metal complex as a side-chain or by the modification of polymers with the metal complex in a post polymerization reaction. While the former strategy can have a highly controlled and quantitative metal complex functionalization, the latter approach is modular, with the potential to attach a library of metal complexes onto the polymer backbone. However, a high yielding orthogonal covalent functionalization is crucial for the success of the modular post polymerization approach. In this contribution we present such a strategy by taking advantage of the 1,3-dipolar cycloaddition, often referred to as “click chemistry”. This transformation is widely used due to its high tolerance to functional groups, high reaction yields, and mild reaction conditions.[8]

Our polymers are based on two different comonomers: styrene and *N*-vinyl carbazole. Styrene was functionalized with azide units for easy, high yielding click reactions with alkyne-containing iridium complexes. The role of the second comonomer, *N*-vinyl carbazole, is manifold. Firstly, poly(*N*-vinyl carbazole) has been employed extensively as a host material in OLEDs due to its hole-transport properties and its high-energy singlet excited state.[9] Moreover, it prevents self quenching and aggregation of metal centers by decreasing the concentration of the iridium complexes along the polymer backbone.

Iridium complexes **1–4**[10,11] and **7**[6] were prepared according to literature procedures. Similar procedures were employed to prepare compounds **5**, **6**, **8**, and **9**. Bimetallic complexes **2** and **3** were reacted with 4-(2-pyridine)benzaldehyde to give **5** and **6**, respectively (Scheme 1). The reductions of **5** and **6** with $LiAlH_4$ yielded the alcohol functionalized complexes **8** and **9**, respectively. Coupling of hex-5-ynoic acid with **7–9** resulted in the formation of complexes **10–12** containing the desired terminal alkyne group. Two different isomers, facial and meridianal, are possible for these complexes. While both isomers can be synthesized selectively using published procedures,[1,2,10] the isomers of interest for OLEDs are the facial ones since their emission quantum yields are significantly higher than the corresponding meridianal isomers.[1] All complexes described in this study are oriented facially as characterized by NMR spectra, emission quantum yields, and emission lifetimes. Furthermore, X-ray crystallography of a single crystal of compound **12** confirms that the three cyclometalating ligands are oriented facially in an octahedral coordination geometry around the metal center as shown in Fig. 1.‡

The synthetic route toward the fully functionalized copolymers is outlined in Scheme 2. To allow for easy characterization, low molecular weight polymers were prepared. *N*-Vinyl carbazole or styrene was copolymerized with *para*-(chloromethyl)styrene (in ratios of 9 : 1) using AIBN as the initiator, yielding **13** (M_n = 4100; PDI = 1.78) and **15** (M_n = 6400; PDI = 1.50), respectively.[5,7] The chloromethylated copolymers were then converted to the corresponding azides **14** and **16** in 90–95% yields. NMR spectroscopy showed that all chlorine units were transformed into the azide groups. Copolymers **14** and **16** were then reacted with complexes **10–12** *via* click chemistry to yield the desired fully functionalized copolymers **17–22** in 71–93% yields. NMR spectra of copolymers **17–22** showed complete conversion of the azide groups to the 1,4-disubstituted 1,2,3-triazoles. Copolymers **17–22** are soluble in common organic solvents such as chloroform and THF.

Table 1 lists the photophysical properties of all copolymers and the corresponding small molecule iridium complex precursors. Fig. 2(a) and 2(b) show the photoluminescence spectra of the alkyne-functionalized complexes **10–12** and copolymers **17–22** in chloroform solutions and the solid state, respectively. UV-vis absorption spectra of **17–22** reveal the characteristic π–π^* transitions originating from the ligands of the iridium complexes

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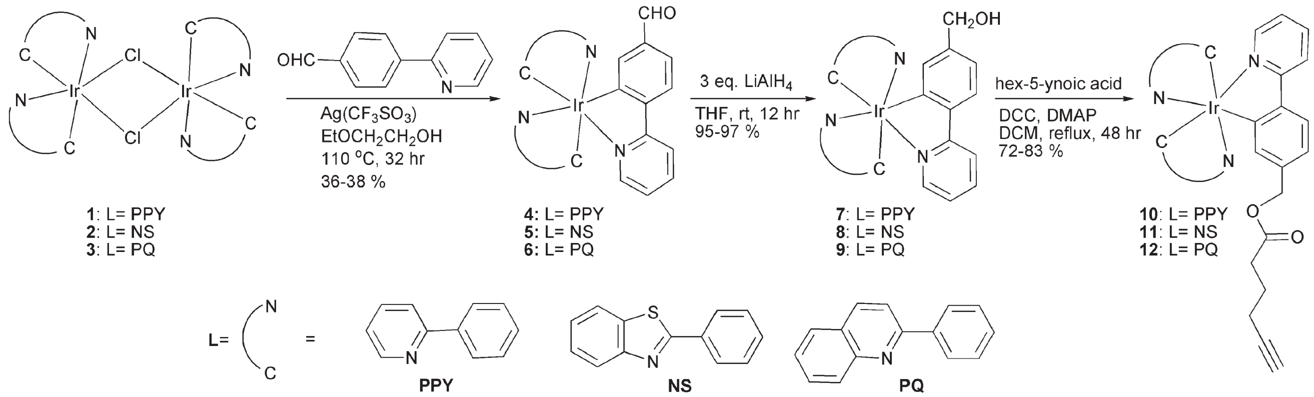


Scheme 1 Synthesis of the alkyne-functionalized iridium complexes **10–12**.

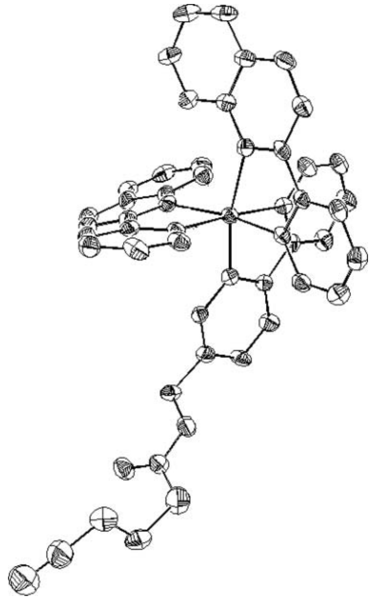
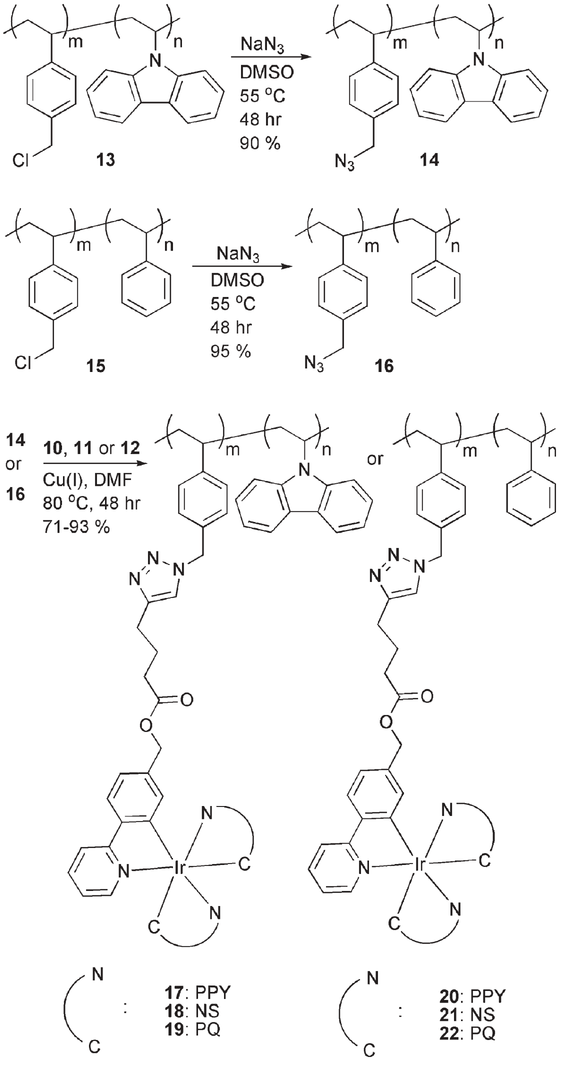


Fig. 1 ORTEP representation of the crystal structure of **12** (50% ellipsoids). Hydrogen atoms are omitted for clarity.

and the carbazole moiety in the high energy region, whereas in the lower energy region, starting around 380 nm and extending to around 500 nm, weak and broad metal-to-ligand charge-transfer (MLCT) transitions of the iridium complexes are observed. Emission maxima of the copolymers are similar to those of the corresponding small molecule iridium complexes. Compared to the solution emissions, the solid state emissions are slightly red shifted for all copolymers (Fig. 2). These results indicate that the polymer backbones do not affect the absorption or emission maxima of the tethered metal complexes. On the other hand, slightly different emission quantum yields are obtained for different polymers in comparison to their small molecule analogues (Table 1). The emission lifetimes of all compounds are strongly affected by the presence of oxygen, which is due to the quenching of the relatively long-lived ^{3}MLCT state by oxygen, causing a decrease in the emission lifetimes. On the other hand, copolymers with and without carbazole groups have similar lifetimes, indicating that there is no emission quenching related to carbazole units.



Scheme 2 Functionalization of the copolymers *via* click chemistry.

In conclusion, using high yielding and fully orthogonal 1,3-dipolar cycloadditions, we have synthesized copolymers with pendant iridium complexes. This functionalization strategy is modular, *i.e.* any alkyne containing the iridium complex can be used. The copolymers retained the optical properties associated with their small molecule analogues both in solution and the solid state. The method described herein offers a straightforward synthesis of functionalized polymeric materials with potential applications in OLEDs.

Table 1 Photophysical data[f] for the alkyne-functionalized iridium complexes **10–12** and copolymers **17–22**

Compound	Solution absorption[a] λ_{max}/nm	Solution emission[a] λ_{max}/nm	Solid emission[b] λ_{max}/nm	Φ^c	τ^d air (deaerated)/ns
10	282, 383, 461[e]	515	517	0.40	34 (1484)
20	282, 384, 461[e]	515	522	0.29	45 (1000)
17	282, 295, 344, 384, 460[e]	515	517	0.40	51 (1297)
11	290, 310, 324, 395, 436[e], 488[e]	554	557	0.36	109 (1612)
21	290, 310, 325, 395, 438[e], 488[e]	555	556	0.22	95 (1393)
18	296, 330, 344, 395, 437[e], 487[e]	554	555	0.19	87 (1485)
12	273, 293, 329, 410, 456[e], 507[e]	597	606	0.11	98 (1735)
22	273, 293, 329, 411, 454[e], 503[e]	606	612	0.07	88 (862)
19	282, 295, 332, 345, 407, 455[e], 511[e]	606	609	0.05	81 (740)

[a] THF solution at rt. [b] Quartz slide at rt. [c] In degassed THF solutions using *fac*-Ir(ppy)$_3$ (Φ = 0.40, in toluene) as standard. [d] Luminescent lifetime in THF solution. [e] Shoulder peak. [f] Luminescence measurements were carried out at λ_{ex} = 380 nm.

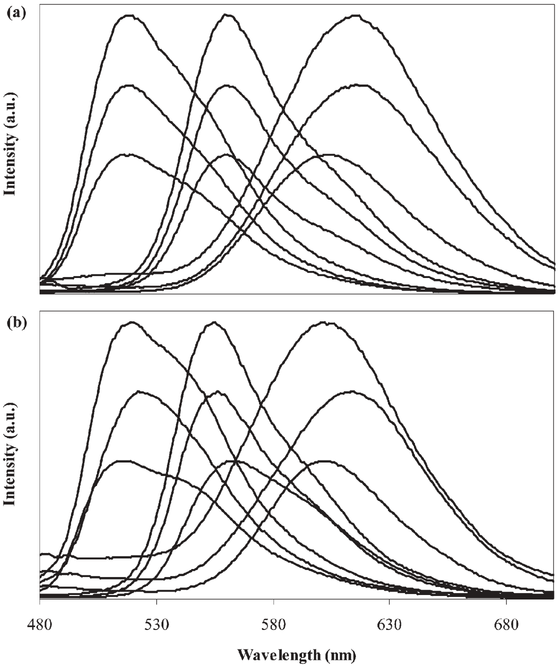


Fig. 2 **(a)** Solution emission (in chloroform) and **(b)** solid state emission spectra of **10–12** and **17–22**. From top to bottom: left curves: **17**, **20**, **10**; middle curves: **18**, **21**, **11**; right curves: **19**, **22**, **12**.

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Notes and references

‡ Crystal data for **12**: $C_{48}H_{36}IrN_3O_2$, M = 879.00. Monoclinic, space group: $P2_1/c$, a = 21.351(3), b = 9.5276(14), c = 18.051(3) Å, β = 96.153(3)°, V = 3650.7(9) Å^3, Z = 4, T = 173(2) K, μ = 3.703 mm^{-1}, R_{int} = 0.1582, R_1 [$I > 2\sigma(I)$] = 0.0668, wR_2 (all data) = 0.1364, GOF = 1.002. CCDC 614840. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609382e

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