Iridium Complexes

Accelerated Discovery of Red-Phosphorescent Emitters through Combinatorial Organometallic Synthesis and Screening**

Nai-Mu Hsu and Wen-Ren Li

Dedicated to Professor Madeleine M. Joullié

The combinatorial approach of synthesis and screening has become the focus of intense interest as a tool for drug discovery in the pharmaceutical industry.[1] Promising developments in medicinal chemistry subsequently pointed the way for material chemists to use this approach to discover diverse catalysts and materials such as liquid crystals[2] and luminescent emitters,[3] among others.[4] Most of these materials are organic compounds. The combinatorial synthesis of organometallic materials is not a common trend yet. Bernhard and co-workers applied the basics of the combinatorial approach to solution synthesis for the discovery of transition-metal-based luminophores.[5] Elsewhere, Binnemans and co-workers coupled luminescent lanthanide(III) complexes on a Merrifield resin through a functionalized ligand.[6] However, a complete combinatorial synthetic sequence and high-throughput screening are yet to be developed to discover organometallic compounds with desired properties.[7]

In the last decade, material chemists have become interested in developing organometallic complexes based on Ir,[8] Os,[9] Ru,[10] and Pt[11] for their applications in organic light-emitting diodes (OLEDs). OLEDs hold great potential for application in flat-panel displays owing to their excellent properties, such as self-luminescence, flexibility, fast response, good contrast, and low energy consumption. Light-emitting materials doped in OLEDs offer an improvement in efficiency and the possibility to tune the color. Fluorescent[12] and phosphorescent emitters with high luminescence efficiencies have been extensively used for this purpose. However, studies have proved that devices based on phosphorescent materials are more efficient than those based on fluorescent materials. For example, bis(2-(2′-benzothienyl)pyridinato-$N,C^{3'}$)-iridium(acetylacetonate) ($[(btp)_2Ir(acac)]$) was used as the dopant for red-light emission and an external quantum

[*] N.-M. Hsu, Prof. Dr. W.-R. Li
    Department of Chemistry and
    Center for Nano Science and Technology
    National Central University
    Chung-Li, Taiwan 32054 (Taiwan)
    Fax: (+ 886) 3-427-7972
    E-mail: ch01@ncu.edu.tw

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efficiency of 6.5% and power efficiency of $2.2\,\mathrm{lm\,W^{-1}}$ at $1\,\mathrm{mA\,cm^{-2}}$ were reported.[8]

Notwithstanding the success in increasing the external quantum efficiency, research on OLEDs is still focused on the improvement of the emission efficiency and the color purity by developing high-efficiency phosphorescent materials on the device architectures. As ligands can affect both the quantum yield and the emission wavelength of iridium complexes significantly, these complexes appear to be excellent candidates to use as electrophosphorescence emitters in OLEDs. Consequently, the development of new organic ligands for iridium complexes is highly desirable in order to maximize the external quantum efficiency and the color purity of devices. On the basis of several studies to improve efficiencies, aminoquinazolines were selected as cyclometalating ligands because of their polarity and potential stability.[8–11] Herein, we report a series of efficient red-phosphorescent emitters discovered by using combinatorial organometallic solid-phase synthesis and screening methodology.

For OLED applications, compounds that emit in a specific color range are desirable. While rational design of compounds with specific emission wavelengths and high quantum yields is difficult, combinatorial solid-phase synthesis appears to be a powerful tool in developing libraries of iridium complexes. The key to discover excellent emitters on solid supports lies in the screening methodology. A crucial feature of the screening methodology is to obtain information about basic photophysical characteristics, namely the wavelength (λ_{em}) and quantum yield (Φ_{PL}) of emission. However, to achieve this aim, the spacer used to link emitters to resins should have no interference in the photophysical characteristics. Hence, the choice of spacer becomes crucial. The use of a conjugated spacer system will affect wavelengths and quantum yields. Saturated alkyl or alkoxy spacers have the advantage of being stable under the reaction sequences. These spacers are non-conjugated systems that allow common solid-phase resins to be used, such as polystyrene-type polymers, in the synthesis of the emitter, an operation that is otherwise impossible owing to the conjugated or aromatic nature of the resins.

Along with the above-mentioned properties, the spacers should mimic aromatic substitution on the heterocyclic system. The selected spacers Ar^m ($m = 1$–3) mimic alkyl phenyl, alkoxy phenyl, and thiophene substitutions, respectively (Figure 1). This strategy of mimicking aromatic substitution in spacers enabled us to process rapid screening. It was found that resin-bound lead compounds $\mathbf{1}(\mathrm{Ar}^m\mathrm{R}^n)$ reveal wavelengths and quantum yields of emission that are very close to those of cleaved products $\mathbf{2}(\mathrm{Ar}^m\mathrm{R}^n)$ and the respective emitters without a spacer, namely $\mathbf{3}(\mathrm{R}^n)$, $\mathbf{4}(\mathrm{R}^n)$, and $\mathbf{5}(\mathrm{R}^n)$ (Figure 1). These spacers also imparted enough flexibility to accommodate the synthesis of a unique bis-cyclometalated $\mathrm{Ir}^{\mathrm{III}}$ μ-chloro-bridged dimer $\mathbf{6}$ (Scheme 1) linked through its four ligands to one resin through spacers. To the best of our knowledge, this kind of assembly has not been reported before.

The parallel solid-phase syntheses (Scheme 1) of resin-bound leads $\mathbf{1}(\mathrm{Ar}^m\mathrm{R}^n)$ and the cleaved products $\mathbf{2}(\mathrm{Ar}^m\mathrm{R}^n)$ were carried out using Wang resin (1% divinylbenzene (DVB) cross-linked; loading: $1.0\,\mathrm{mmol\,g^{-1}}$). Wang resin was
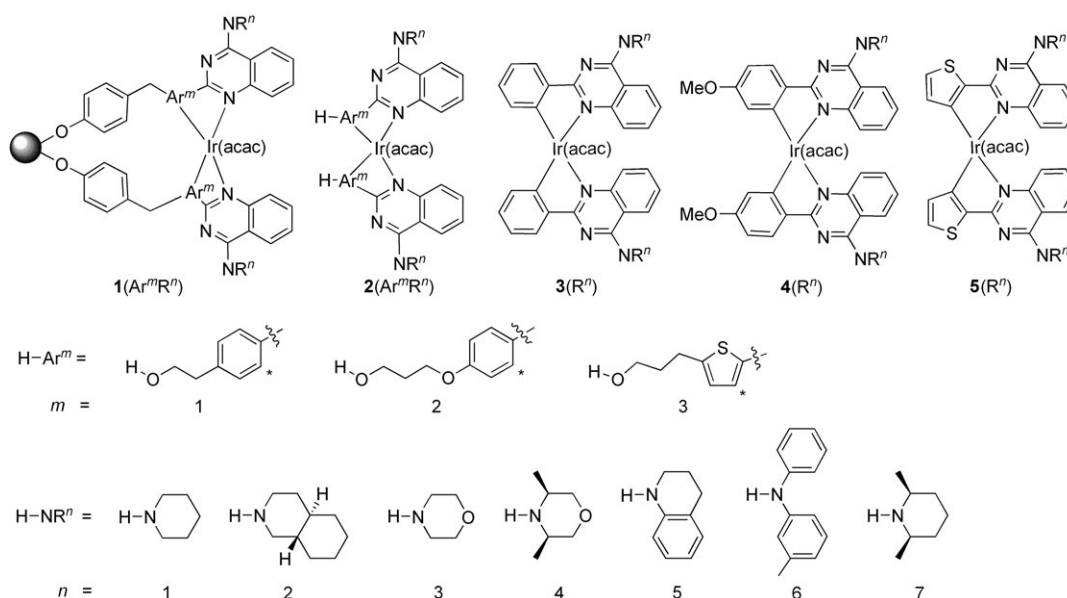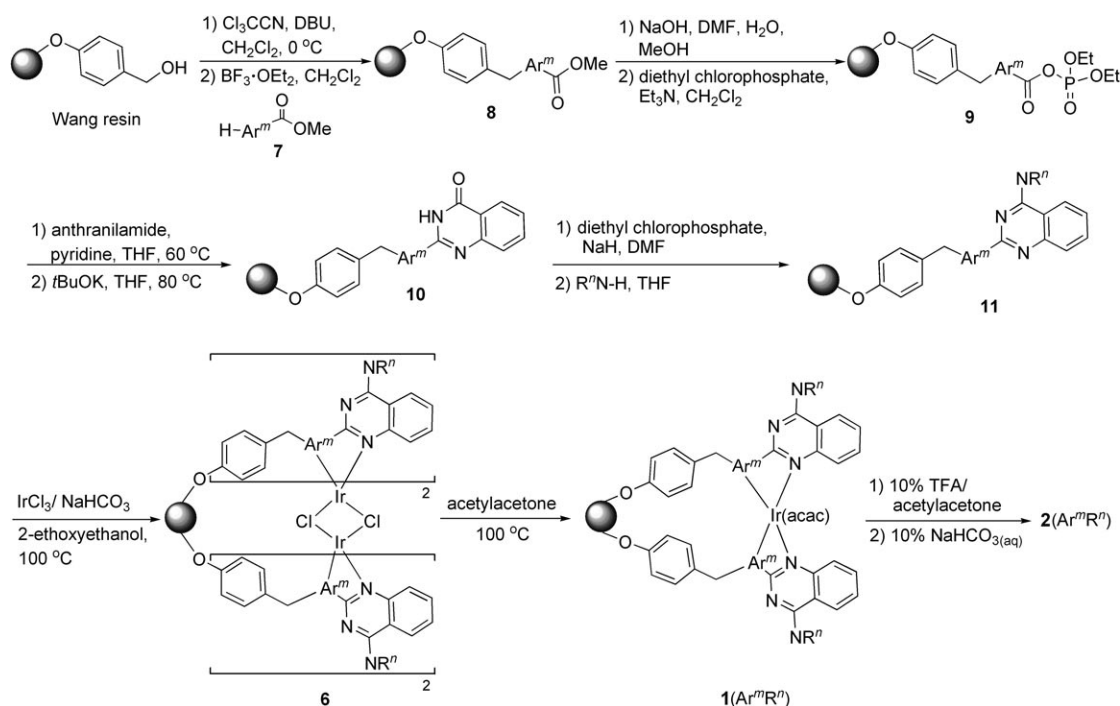
Figure 1. General structures of leads **1**(Ar^{m}R^n), cleaved products **2**(Ar^{m}R^n), and emitters **3**(R^n)–**5**(R^n). The aryl group binds to Ir through the positions marked with an asterisk in Ar^m. acac = acetylacetonate

Scheme 1. Solid-phase synthesis of leads **1**(Ar^{m}R^n) and cleaved products **2**(Ar^{m}R^n). DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DMF = N,N-dimethylformamide; TFA = trifluoroacetic acid.

activated as its trichloroacetimidate and linked with the derivatives **7** through their hydroxy groups to obtain the resin-bound esters **8**.[13] Hydrolysis of esters **8** was carried out using sodium hydroxide in the presence of DMF, MeOH, and water, and the resulting acids were derivatized as mixed anhydrides **9**.[14] Anthranilamide was coupled with anhydrides **9** to give N-acylated products, which were cyclized under basic conditions to afford the resin-bound quinazolin-4-one derivatives **10**. Of the various bases tested,[15] *t*BuOK was found to be the

best and was employed in the synthesis of the library. Resins **10** were treated with sodium hydride followed by diethyl chlorophosphate, and the resulting *o*-phosphorylated products were reacted with R^{n}NH to give the resin-bound quinazolines **11**.[16] During the synthetic sequences, at several stages, a small portion of the compounds was taken out and either monitored by magic-angle spinning gel-phase NMR spectroscopy or cleaved to check whether the reaction had gone to completion. Whenever necessary, the previous steps

were repeated. The purity (> 50 %) of compounds **11** was crucial for the success of the following organometallic reactions. The resins **11** were treated with iridium trichloride hydrate in the presence of NaHCO$_3$ and 2-ethoxyethanol to give the dimers **6**.[8,17] The formation of the chloro-bridged dimer **6** linked through its four ligands through spacers to form a polymer-bound complex within the same resin was proved by analysis of the polarized optical microscope picture. Ir^{III} μ-chloro-bridged dimers **6** were sensitive to pH at high temperature. The pH value was maintained around 7 by adding NaHCO$_3$ to avoid decomposition of the dimers. Further treatment of the resins with acetylacetone afforded the desired iridium complexes **1**.[18]

The polymer-bound lead complexes **1** are stable in air, and no decomposition was noted over the period of 3 months at room temperature. When 10, 20, and 40 % trifluoroacetic acid (TFA) in CH$_2$Cl$_2$ or 2-ethoxyethanol was employed to cleave resin **1**, decomposition of the iridium complexes was observed. However, 10 % TFA in acetylacetone followed by treatment with aqueous NaHCO$_3$ (10 %) was found to be adequate to cleave the resin completely while keeping the iridium complex intact to afford products **2**. The compounds **2** were purified by normal-phase HPLC and obtained in 30–45 % yields from the Wang resin, which corresponds to about 90 % yield per transformation in this 12-step solid-phase procedure. This range of yields is enough to measure photophysical properties because only a very low concentration of the complexes in the polymer is required for luminescence to be studied. Moreover, problems with concentration quenching would probably arise when the concentration of the complex on the polymer is too high.

The combinatorial technique does not carry full merits if the rapid synthesis is not accompanied with the facile and speedy method of screening synthesized libraries for the desired properties. Combinatorial screening using a microplate reader was developed to search for highly luminescent materials from the synthesized library of the resin-bound compounds **1**, **6**, **10**, and **11**. Screening of a few representative resin-bound leads is displayed in Figure 2, and their emission maxima are summarized in Tables 1 and 2. The resin-bound leads of significant interest were cleaved to afford compounds **2**, and the corresponding emitters **3–5** were prepared by using a similar protocol to that described in Scheme 1. These three groups, namely resin-bound leads **1**, cleaved products **2**, and emitters **3–5**, were compared for their photophysical properties (Table 2). Table 1, which lists the wavelengths of resin-bound organic compounds **1 A–3 F**, indicates that the screening method (Figure 2) used here should be suitable to identify fluorescent organic emitters. Also during the reaction sequence the purity of chloro-bridged dimer **6** (4 A–6 C) and the completion of previous reaction step was assured by the disappearance of the emission between 400 and 500 nm. Analysis of the quantitative photophysical properties data (Table 2, 6 D–8 F) showed that the deviations in emission maxima of leads **1**, cleaved products **2**, and the corresponding emitters **3–5** are within a very narrow range of 11 nm. In addition, the quantum yields[19] of the products **2** and those of emitters **3–5** differ from each other by only 0.08. When wavelengths are close, the brightness of resin-bound leads **1**
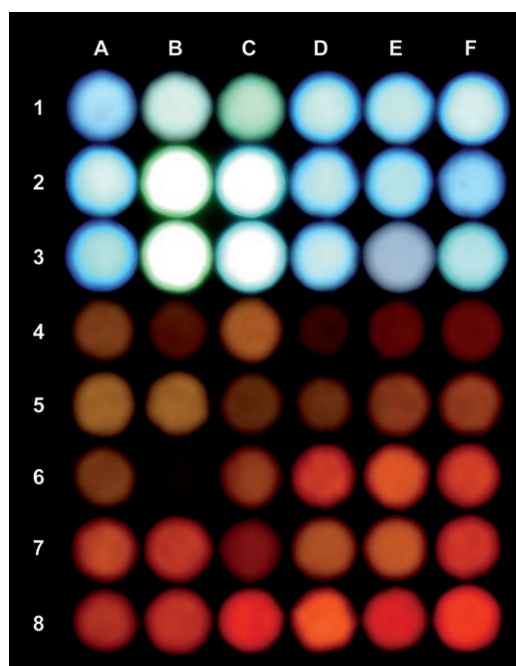

Figure 2. Screening of a library of representative resin-bound leads (see Tables 1 and 2).

Table 1: Emission maxima of resin-bound compounds **6**, **10**, and **11**.

Resin[a]	Compound	λ_{em} [nm]	Resin[a]	Compound	λ_{em} [nm]
1 A	**10**(Ar^1)	514	3 F	**11**(Ar^{3}R^7)	488
1 B	**10**(Ar^2)	522	4 A	**6**(Ar^{1}R^1)	585
1 C	**10**(Ar^3)	541	4 B	**6**(Ar^{1}R^2)	600
1 D	**11**(Ar^{1}R^1)	470	4 C	**6**(Ar^{1}R^3)	604
1 E	**11**(Ar^{1}R^2)	440	4 D	**6**(Ar^{1}R^4)	599
1 F	**11**(Ar^{1}R^3)	456	4 E	**6**(Ar^{1}R^5)	605
2 A	**11**(Ar^{1}R^4)	472	4 F	**6**(Ar^{1}R^6)	619
2 B	**11**(Ar^{1}R^5)	507	5 A	**6**(Ar^{2}R^1)	578
2 C	**11**(Ar^{1}R^6)	528	5 B	**6**(Ar^{2}R^2)	580
2 D	**11**(Ar^{2}R^1)	528	5 C	**6**(Ar^{2}R^3)	573
2 E	**11**(Ar^{2}R^2)	436	5 D	**6**(Ar^{2}R^4)	590
2 F	**11**(Ar^{2}R^3)	400	5 E	**6**(Ar^{2}R^5)	604
3 A	**11**(Ar^{2}R^4)	435	5 F	**6**(Ar^{2}R^6)	615
3 B	**11**(Ar^{2}R^5)	515	6 A	**6**(Ar^{3}R^3)	614
3 C	**11**(Ar^{2}R^6)	485	6 B	**6**(Ar^{3}R^6)	644
3 D	**11**(Ar^{3}R^3)	421	6 C	**6**(Ar^{3}R^7)	613
3 E	**11**(Ar^{3}R^6)	476			

[a] Refers to Figure 2.

are proportionally correlated with quantum yields of the cleaved products **2** and the respective emitters **3–5**. This result can be seen from Figure 2 and Table 2 by comparing leads **1** [7B: **1**(Ar^{1}R^5); 8B: **1**(Ar^{2}R^5); 8C: **1**(Ar^{2}R^6); 8F: **1**(Ar^{3}R^7)], cleaved products **2** [**2**(Ar^{1}R^5); **2**(Ar^{2}R^5); **2**(Ar^{2}R^6); **2**(Ar^{3}R^7)], and the respective emitters **3–5** [**3**(R^5); **4**(R^5); **4**(R^6); **5**(R^7)]. Moreover, spectral characteristics (Figure 3) observed for the above-mentioned three groups of compounds (**1**, **2**, and **3–5**) further validated the screening protocol. The full width at half maximum (FWHM) and shapes of the emission spectra are very similar in each case for the compounds on beads, the respective cleaved products, and corresponding emitters. Thus, naked-eye observation of the brightness coupled with

Table 2: A comparison of the photophysical properties of resin-bound leads **1**(Ar^{m}R^n), cleaved products **2**(Ar^{m}R^n), and emitters **3**(R^n)–**5**(R^n).

| Resin[a]	Leads **1**	λ_{em} [nm]	Products **2**	λ_{em} [nm]	Φ_{PL}	Emitters	λ_{em} [nm]	Φ_{PL}
6 D	**1**(Ar^{1}R^1)	598	**2**(Ar^{1}R^1)	594	0.52	**3**(R^1)	598	0.54
6 E	**1**(Ar^{1}R^2)	594	**2**(Ar^{1}R^2)	592	0.48	**3**(R^2)	595	0.49
6 F	**1**(Ar^{1}R^3)	590	**2**(Ar^{1}R^3)	590	0.47	**3**(R^3)	595	0.46
7 A	**1**(Ar^{1}R^4)	601	**2**(Ar^{1}R^4)	598	0.36	**3**(R^4)	600	0.35
7 B	**1**(Ar^{1}R^5)	625	**2**(Ar^{1}R^5)	624	0.28	**3**(R^5)	628	0.24
7 C	**1**(Ar^{1}R^6)	632	**2**(Ar^{1}R^6)	637	0.27	**3**(R^6)	643	0.31
7 D	**1**(Ar^{2}R^1)	588	**2**(Ar^{2}R^1)	588	0.37	**4**(R^1)	588	0.41
7 E	**1**(Ar^{2}R^2)	590	**2**(Ar^{2}R^2)	585	0.37	**4**(R^2)	586	0.41
7 F	**1**(Ar^{2}R^3)	592	**2**(Ar^{2}R^3)	592	0.51	**4**(R^3)	592	0.49
8 A	**1**(Ar^{2}R^4)	591	**2**(Ar^{2}R^4)	587	0.37	**4**(R^4)	590	0.45
8 B	**1**(Ar^{2}R^5)	619	**2**(Ar^{2}R^5)	624	0.35	**4**(R^5)	627	0.31
8 C	**1**(Ar^{2}R^6)	630	**2**(Ar^{2}R^6)	634	0.58	**4**(R^6)	633	0.62
8 D	**1**(Ar^{3}R^3)	616	**2**(Ar^{3}R^3)	613	0.46	**5**(R^3)	612	0.50
8 E	**1**(Ar^{3}R^6)	655	**2**(Ar^{3}R^6)	652	0.24	**5**(R^6)	653	0.24
8 F	**1**(Ar^{3}R^7)	635	**2**(Ar^{3}R^7)	636	0.69	**5**(R^7)	636	0.67

[a] Refers to Figure 2.
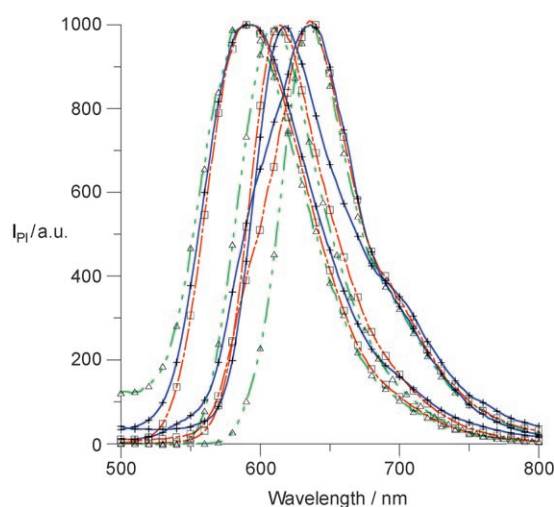
Figure 3. A comparison of the photoluminescence (PL) spectra of resin-bound leads **1**, cleaved products **2**, and emitters **4**–**5**. Emission maxima are provided in parentheses (λ_{em} [nm]): Blue line (+): **1**(Ar^{2}R^3) (592); **1**(Ar^{3}R^3) (616); **1**(Ar^{3}R^7) (635). Red line (□): **2**(Ar^{2}R^3) (592); **2**(Ar^{3}R^3) (613); **2**-(Ar^{3}R^7) (636). Green line (△): **4**(R^3) (592): **5**(R^3) (612): **5**(R^7) (636). $\lambda_{ex} = 370$ nm.

the determination of emission maxima on beads before cleavage can lead to the identification of potentially bright light-emitting hits. By using this combinatorial screening technique, two optimum red emitters **4**(R^6) and **5**(R^7) were identified.

To evaluate the electroluminescent properties of the identified hits, several electroluminescent (EL) devices were fabricated using these iridium complexes as dopant emitters. The electroluminescent characteristics of **4**(R^6) and **5**(R^7) are summarized in Table 3. In devices **A**–**F**, **4**(R^6) and **5**(R^7) were doped into a light-emitting

layer at a concentration of 8% to afford the optimum external quantum efficiency. Device **B** shows excellent electroluminescent characteristics for OLEDs deposited with a 50-nm-thick layer of Alq. A maximum external quantum efficiency of 15.2% and a power efficiency of 10.0 lm W^{-1} were obtained at 4.5 V. The device also emitted strong red light at 630 nm with a maximum brightness of 54919 cd m^{-2} at 18.0 V. Device **F** was prepared using **5**(R^7) as the dopant emitter in the CBP layer and using a 60-nm-thick layer of deposited Alq. The device revealed an emission maximum at 630 nm, external quantum efficiency of 20.3%, current efficiency of 16.6 cd A^{-1}, and power efficiency of 12.2 lm W^{-1} at 4.25 V. The corresponding CIE (Commission Internationale de l'Eclairage) coordinates are $x = 0.649$, $y = 0.349$ for **4**(R^6) in device **B**, and $x = 0.666$, $y = 0.332$ for **5**(R^7) in device **F**, which coincide with the National Television Standards Committee (NTSC) red specification.

In conclusion, we have demonstrated that a rapid combinatorial synthesis and screening methodology can be successfully applied to discover luminescent materials. This efficient synthetic protocol has been applied to prepare a library of new red-phosphorescent Ir complexes through assembly of a novel resin-bound bis-cyclometalated Ir^{III} μ-chloro-bridged dimer. The spacers used adequately mimicked alkyl or alkoxy substitutions on aromatic heterocyclic ligand systems and imparted enough flexibility. The photophysical

Table 3: Electrophosphorescence data for iridium complexes **4**(R^6) and **5**(R^7).[a]

Device	Device structure	V [V]	η_{ext} [%]	η_c [cd A^{-1}]	η_p [lm W^{-1}]	CIE (x,y)
A	ITO/α-NPB (60 nm)/**4**(R^6):CBP (8%, 30 nm)/ BCP (30 nm)/Alq (40 nm)/LiF (0.5 nm)/Al	4.75	13.8	13.6	9.0	0.647, 0.351
B	ITO/α-NPB (60 nm)/**4**(R^6):CBP (8%, 30 nm)/ BCP (30 nm)/Alq (50 nm)/LiF (0.5 nm)/Al	4.5	15.2	14.9	10.0	0.649, 0.349
C	ITO/α-NPB (60 nm)/**4**(R^6):CBP (8%, 30 nm)/ BCP (30 nm)/Alq (60 nm)/LiF (0.5 nm)/Al	5.0	15.4	13.8	8.7	0.651, 0.347
D	ITO/α-NPB (60 nm)/**5**(R^7):CBP (8%, 30 nm)/ BCP (30 nm)/Alq (40 nm)/LiF (0.5 nm)/Al	4.25	18.9	17.8	13.2	0.661, 0.337
E	ITO/α-NPB (60 nm)/**5**(R^7):CBP (8%, 30 nm)/ BCP (30 nm)/Alq (50 nm)/LiF (0.5 nm)/Al	4.0	19.6	17.1	13.4	0.665, 0.334
F	ITO/α-NPB (60 nm)/**5**(R^7):CBP (8%, 30 nm)/ BCP (30 nm)/Alq (60 nm)/LiF (0.5 nm)/Al	4.25	20.3	16.6	12.2	0.666, 0.332

[a] ITO: indium tin oxide; α-NPB: *N,N*'-di(naphthalen-1-yl)-*N,N*'-diphenylbenzidine; CBP: 4,4'-*N,N*'-dicarbazolebiphenyl; BCP: 2,9-dimethyl-7-diphenyl-1,10-phenanthroline; Alq: tris(8-hydroxy-quinolina-to)aluminum. The data for external quantum efficiency (η_{ext}), current efficiency (η_c), and power efficiency (η_p) are the maximum values of the device.

properties that were measured for this library of emitters were astonishingly accurate considering that the resins were analyzed directly. The strong coherence among the data from resin-bound leads, cleaved products, and corresponding emitters confirm that luminescent properties of pure emitter complexes can be predicted directly by screening resins. Our screening data analysis also resulted in the identification of two hits with high quantum yields. The EL devices based on these complexes emitted saturated red electroluminescence with high quantum efficiency and power efficiency and satisfied NTSC red specifications. The present solid-phase synthetic methodology and screening technique are not only useful for accelerating the discovery of luminescent complexes but also may find broad applications in the field of organometallics and combinatorial chemistry.

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