ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Rapid Combinatorial Synthesis and Chromatography Based Screening of Phosphorescent Iridium Complexes for Solution Processing

*Andreas Hohenleutner, Susanna Schmidbauer, Rudolf Vasold, Dominik Joosten, Philipp Stoessel, Herwig Buchholz, and Burkhard König**

This work reports the combinatorial synthesis and screening of phosphorescent iridium complexes as solution processable emitters for OLEDs. The approach taken here allows for the rapid synthesis, isolation, spectroscopic characterization and identification of the libraries based on chromatographic methods. Subsequent analysis of the irradiation induced degradation provides insight on the stability of the complexes under continuous excitation. The method is versatile and can easily be applied to other metal complexes or organic dyes for various applications, e.g., in electroluminescence, photovoltaics and sensing.

1. Introduction

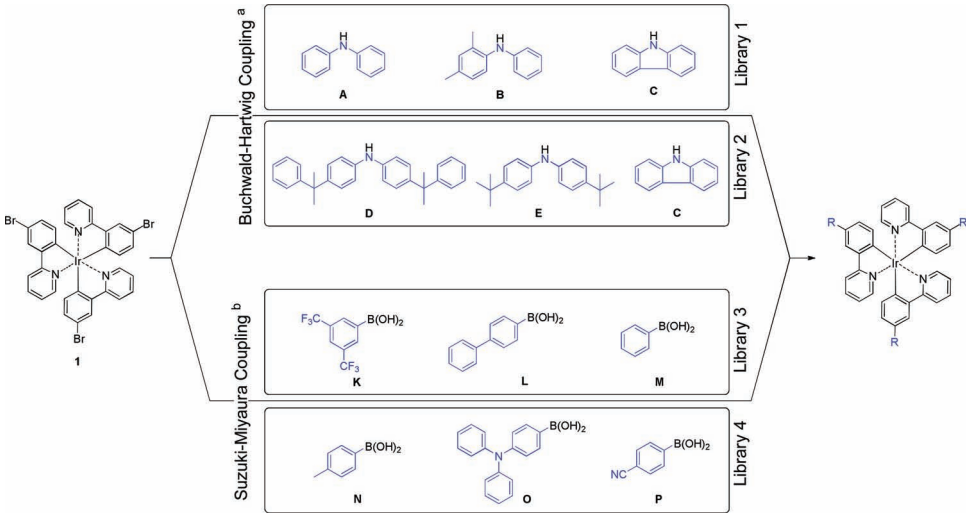
Iridium complexes have been employed as dyes for biological labeling[1] and sensing of different analytes,[2] as photon upconversion agents,[3] dyes for dye-sensitized solar cells (DSSCs),[4] photocatalysts for CO_2 reduction and water splitting[5] and more recently as efficient catalysts in the emerging field of organo photoredox catalysis.[6] While their unique properties make them promising candidates in all of the above mentioned areas, their current most important application is their use as emitters in organic light-emitting devices (OLEDs). Spurred by the discovery of the triplet harvesting effect by Forrest et al. in 1998,[7] enabling a theoretical internal quantum efficiency of 100%, the number of reported phosphorescent iridium complexes has grown significantly over the last decade. The preference of cyclometallated iridium complexes for OLED applications can be rationalized by their extremely high triplet quantum yields,[8] the predictability and tunability of their emission color over the whole visible spectrum, good thermal and photo-stability compared to other transition metal complexes as well as their good synthetic accessibility.[9] For OLEDs produced via thermal vapor deposition, the excellent performance of these devices has already allowed the technology to enter mass production. However, there are still important challenges to be met. Even though there has been substantial progress in improving the operational lifetime of phosphorescent emitters, further improvement in the stability of these materials is highly desirable to obtain highly efficient and long term stable devices. To realize large area display and lighting applications at a competitive price, it is furthermore of interest to develop materials with sufficient solubility in suitable solvents to enable processing from solution for example via ink jet printing.

While modern computational methods can provide reliable information on the emission colors and energy,[10] the color purity and in particular the stability of the iridium complexes cannot be predicted in such a straightforward fashion. To deepen the understanding of these compounds and gain insight into structure-property relationships concerning those essential criteria, it is still necessary to synthesize and characterize a large number of compounds.

While combinatorial chemistry is a well established tool for the rapid synthesis of potential biologically active molecules[11] or catalysts[12] there have been surprisingly few reports of combinatorial methods for the synthesis and screening of new phosphorescent emitters for OLEDs. Bernhard et al. reported the parallel synthesis of a number of iridium complexes and the screening of their photophysical properties directly from the reaction mixture, omitting any purification steps.[10e] In 2006, Li et al. synthesized a library of iridium complexes by parallel solid phase synthesis and identified possible hits via their "on bead" emission.[13] Recently then, Nazeeruddin et al. prepared a library of 90 heteroleptic complexes via a similar approach as Bernhards with a slightly modified procedure at room temperature.[14] However, as the purity of materials is absolutely vital for the operational device lifetime, the laborious, time consuming and therefore expensive purification of potential new emitters is still inevitable to obtain information about the stability of those compounds. Since the rapid purification of

A. Hohenleutner, S. Schmidbauer,
Dr. R. Vasold, Prof. B. König
Institut für Organische Chemie
Universität Regensburg
Universitätsstraße 31, D-93053 Regensburg, Germany
E-mail: burkhard.koenig@chemie.uni-regensburg.de
Dr. D. Joosten, Dr. P. Stoessel, Dr. H. Buchholz
Merck KGaA, Performance Materials Division
Location F61/383, Frankfurter Str. 250,
D-64293 Darmstadt, Germany

DOI: 10.1002/adfm.201200397



Scheme 1. Synthesis of libraries 1–4. Reaction conditions: a) $Pd(OAc)_2$, $P(^tBu)_3$, NaO^tBu, toluene/dioxane, 130 °C, 4 h. b) $Pd(OAc)_2$, P(o-tolyl)$_3$, K_3PO_4, toluene/dioxane/water, 85 °C, 10 h.

combinatorial libraries via chromatographic methods is a well established technique in pharmaceutical industry,[15] we have developed a screening for phosphorescent iridium complexes based on this methodology. Having a small amount of the purified compounds available, we can determine the photophysical properties of the new compounds and initially assess their stability under continuous excitation.

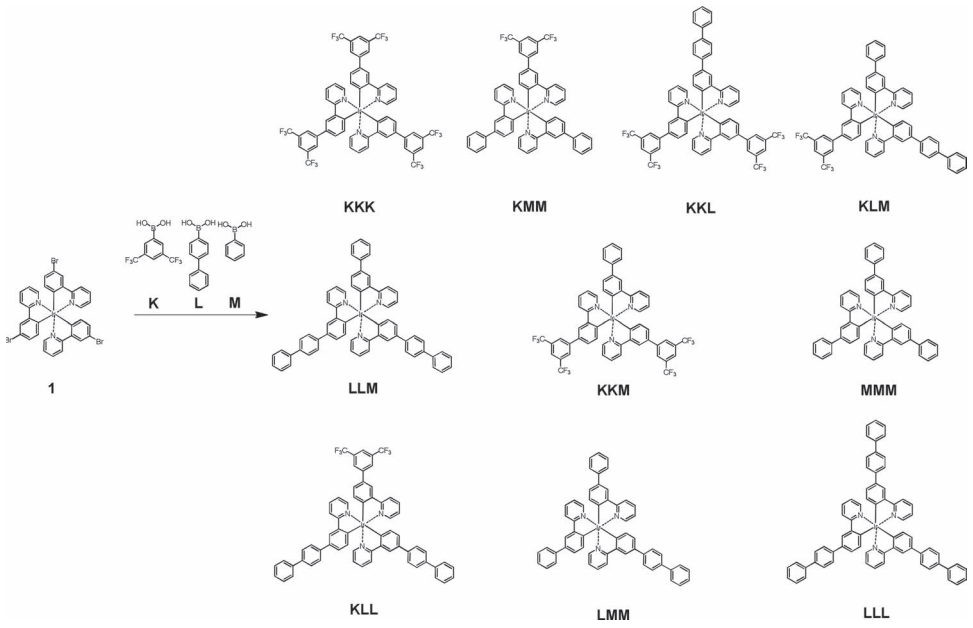
2. Results and Discussion

2.1. Synthesis

To develop the combinatorial synthesis and screening we chose to focus on structures derived from the epitomal $Ir(ppy)_3$ which despite being one of the first reported[16] phosphorescent emitters remains to be one of the most efficient and widely used dopants for phosphorescent OLEDs to date.[17] Incorporation of suitable dendritic structures at the periphery of an emitter is known to provide benefits to the original phosphorescent emitter: self quenching can be suppressed via shielding of the emissive core by branched side chains. Following this strategy, high solid state quantum efficiencies were obtained using ethylhexyloxy chains as dendritic structures.[9a] However, this benefit was limited by the fact that charge-carrier mobility and glass transition temperature T_g may be decreased. These drawbacks could be eliminated using arylated dendrons.[18] Another advantage using these structures is the enhanced solubility for a better compatibility regarding solution processing. Utilizing palladium mediated C-C and C-N coupling reactions (Buchwald-Hartwig and Suzuki-Miyaura respectively), arylated dendritic structures can be attached to the emitting iridium core starting from the Br-functionalized $Ir(ppy)_3$ derivative **1**[19] in order to obtain efficient and soluble phosphorescent emitters in excellent yields and purity.[20] The method is particularly advantageous for a combinatorial approach, as the introduction of structural diversity takes place in the last step of the synthesis. The time consuming preparation and purification of a variety of ligands can thus be avoided as boronic acids and diarylamines are widely available from commercial suppliers. Utilizing this post modification procedure, we synthesized 4 libraries, two of them via a Buchwald-Hartwig protocol and two via Suzuki-Miyaura reactions (**Scheme 1**). For each of the libraries we combined precursor **1** with three different amines/boronic acids in a one-pot reaction, giving way to a total of 10 possible products per reaction. **Scheme 2** exemplarily shows the synthesis of library 3 with all possible products. We assigned a letter to each of the coupling partners, so that all compounds prepared via the combinatorial approach can be described by a three letter code - each letter representing one introduced substituent. **MMM** for example is the compound where all three bromine functionalities have been replaced by a phenyl group via the Suzuki coupling with phenylboronic acid **M**. This combinatorial strategy facilitates the rapid generation of a large number of structurally diverse compounds as it enables the synthesis of up to 10 products with only one reaction to be performed. As a control, we synthesized and characterized several homoleptic reference complexes via conventional reactions. Their absorption and emission spectra were recorded and showed excellent agreement with the ones obtained from the combinatorial synthesis and screening.

2.2. Screening

To enable the separation and characterization of the compounds in our libraries on a suitable timescale, a chromatography based screening was developed. **Figure 1** outlines the screening setup. In a first step, the crude reaction mixture is separated via a semipreparative HPLC system. A diode array detector (DAD) and a



Scheme 2. Synthesis of library 4 with all 10 expected products.

fluorescence detector (FLD) allow a peak based automated fraction collection and the simultaneous recording of absorption and phosphorescence spectra. **Figure 2** shows 3D-absorption- and emission-plots obtained from the separation of library 2. The eluted compounds were collected into vials, quantified and identified via LC-MS and then subjected to repeated irradiation and HPLC analysis to investigate the irradiation induced degradation of the compounds.

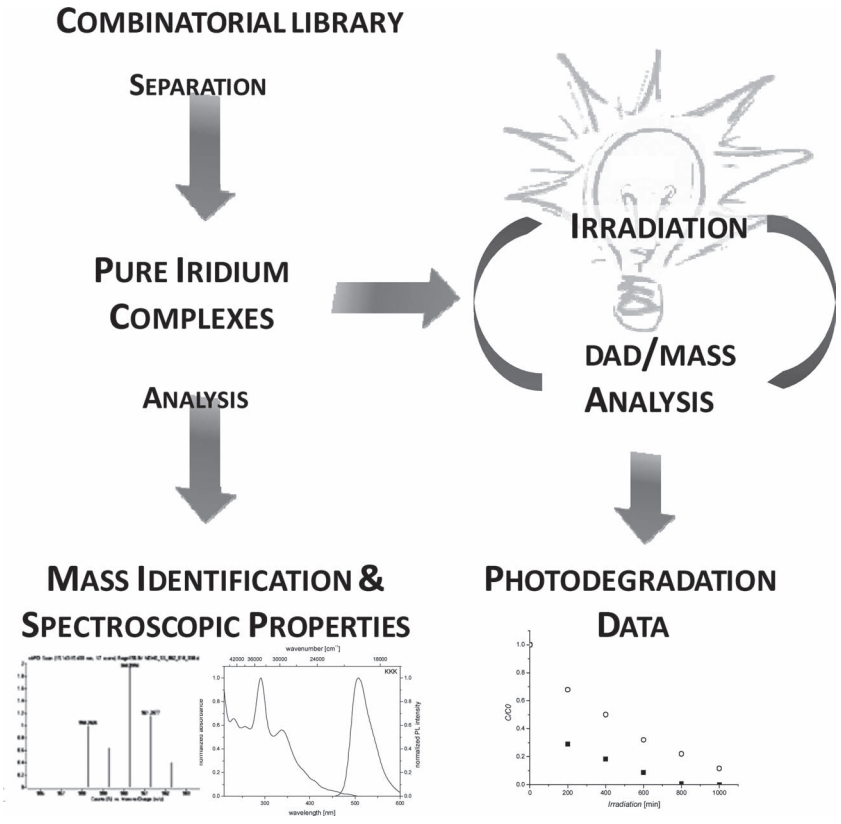


Figure 1. Schematic representation of the purification and screening process.

2.3. Separation and Spectroscopic Properties

Of the 40 theoretically possible compounds, 36 could be separated and identified via LC-MS. The yields for the single compounds were estimated via the integrated area obtained from the chromatograms at 305 nm, assuming similar molar absorption coefficients for the different compounds. Apart from library 2 which showed a nearly statistical distribution of products, no clear trends in the reactivity of reactants could be elucidated.[21] Their absorption and emission spectra (see the supporting information) were recorded and the full width at half maximum (FWHM) was determined as an indicator of color purity. **Table 1** gives an overview of all identified compounds, their maximum emission wavelengths and FWHM values as well as the m/z values obtained by LC-MS analysis.

While the complexes prepared via the Suzuki couplings all emit in the green region, introduction of the electron donating arylamine moieties para to the metal leads to a significant bathochromic shift of the emission wavelength into the orange region. This

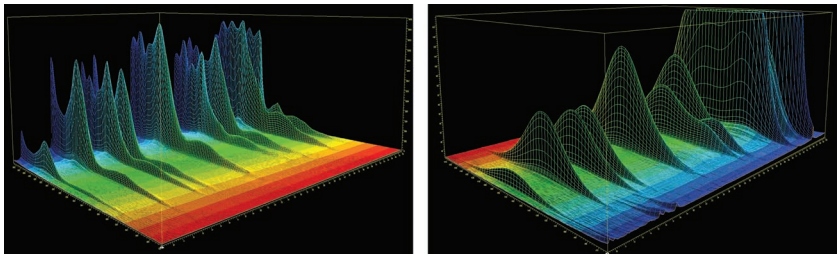


Figure 2. 3D-Plots from the separation of library 2. Left: Absorption intensity (z-axis) plotted against the wavelength (y-axis) and retention time (x-axis). Right: Emission intensity (z-axis) plotted against the wavelength (y-axis) and retention time (x-axis). The colors do not represent the colors as perceived by the eye.

is caused by the electron donating effect of the arylamine substituents, effectively increasing the donation to the metal via the Ir-C bond, destabilizing the metal centered HOMO and thus reducing the HOMO-LUMO energy gap. The same trend, although not as pronounced, could also be observed depending on the substituents of the aryl or diarylamine groups. Increasing electron donating character leads to a red shifted emission while electron withdrawing substituents cause a blue shift of the emission maximum (**Figure 3**). The electronic influence of the substituents on the emission energy can be rationalized using Hammett parameters for para substitution. Plotting the emission maxima against σ_{para} of the substituents shows a good correlation with the notable exception of carbazole (Figure 3).

To gain further insight on the photophysical properties of the compounds we also estimated the phosphorescence quantum yields Φ_P of the complexes relative to a standard in a separate experiment. The obtained Φ_P values vary greatly from 0.17 to 0.82. The compounds can be divided into two categories according to their quantum efficiencies: The first group exhibits good to excellent Φ_P values of 0.54–0.85 and consists of the complexes obtained via the Suzuki-Miyaura reactions as well as the fully carbazole substituted **CCC.** The second group - obtained via Buchwald-Hartwig couplings - has diarylamine substituents and exhibits smaller Φ_P values between 0.17 and 0.25.

It is well established that motional relaxation can be responsible for non radiative transitions and that in return enhanced molecular rigidity and restricted intramolecular motion results in improved radiative rates.[9a] Ono et al. examined the influence of different hole trapping moieties such as diphenylamine, carbazole and phenoxazine on $Ir(ppy)_3$ based complexes with the phenylpyridine ligands substituted at the 4-position of the phenyl ring.[22] They found significantly lower quantum yields for the conformationally free diphenylamine substituted compounds while the more rigid carbazole substituent gave an excellent Φ_P. These observations are in good agreement with our obtained quantum yields for **CCC** (Φ_P = 0.82) and **AAA** (Φ_P = 0.25). This trend continues when looking at the different arylamine substituents in relation to each other - the higher the conformational flexibility of the arylamine substituents, the lower the Φ_P values seem to be. Compounds containing flexible substituents such as dimethylbenzyl (**D**) or *tert*-butyl (**E**) (Φ_P = 0.17–0.19) show slightly reduced phosphorescence efficiencies compared to the methyl- or non-substituted diphenylamines **A** and **B** (Φ_P ~ 0.25). Interestingly, the substitution with triphenylamine (**O**) did not lead to a significant reduction of Φ_P which indicates that the introduction of flexibility on the periphery of the molecule further away from the emitting center does not significantly reduce the quantum yields. Since the introduction of structurally flexible substituents is a common strategy for increasing solubility, this antagonistic relationship between conformational flexibility and phosphorescence efficiency should be kept in mind when designing emitters suitable for solution processing. Increasing the solubility by introducing flexibility at the periphery while preserving the rigidity near the emitting center could therefore be a promising strategy for realizing highly efficient phosphorescence from soluble molecules.

Interesting effects could be observed regarding the emission characteristics of heteroleptic compounds containing ligands of different energies: Compounds with two arylamine and one carbazole substituents show emission that seems to be dominated by the lower energy transition centered on the arylamine substituted ligand, manifesting in emission maxima around 570–575 nm and quantum yields between 0.17 and 0.25.

For complexes containing two carbazoles as well as one arylamine substituent, dual emission effects could be observed: While compounds **CCE** (**E** = bis(4-tert-butylphenyl)amine) and **CCA** (**A** = diphenylamine) exhibit an orange emission with a small shoulder in the green region (**Figure 4**), complex **CCD** containing two carbazole and one 4,4′-bis(α,α-dimethylbenzyl)-diphenylamine (**D**) substituent shows green phosphorescence with a shoulder in the orange region. To gain more information on this pronounced difference in the emission behavior of **CCD** and **CCE**, we synthesized **DDD** (which could not be obtained from the chromatographic separation of library 2) via a conventional reaction and determined its quantum yield. Φ_P (**DDD**) was found to be 0.20, which is similar to that of **EEE** (Φ_P = 0.18). Since these emission efficiencies are quite similar, the reasons for the different phosphorescence characteristics must lie elsewhere. Detailed spectroscopic investigations might provide a deeper insight into this phenomenon in the future. Emitters with dual emission properties exhibit broad banded emission making them very promising candidates for white organic light-emitting diodes.[23] The combinatorial synthesis of focused libraries directed at the tuning of dual emission properties could be a valuable tool to facilitate the development of new emitters in this field.

2.4. Photodegradation Studies

While there is still not much known about the exact degradation mechanisms of emitters in PhOLEDs, most recent investigations suggest an important role of excited states.[24] Population of higher lying thermally accessible states for example may lead to bond rupture and possibly cause ligand dissociation.[25] Researchers at Fujifilm already used the analysis of irradiation induced degradation as a tool to assess the stability of new emitters. They successfully identified a new long lived

Table 1. Overview over all synthesized complexes with their yields, maximum emission wavelengths, FWHM values, PL quantum yields as well as the m/z (100%) values obtained via LC-MS.

	Code	Formula	m/z (100%)[a]	λ_{max} [nm]	FWHM [nm]	Quantum yield[b]	Yield [%][c]
Library 1	AAB	$IrC_{71}H_{55}N_6$	1185.4227 (M+H)+	571	59	0.24	6
	BBC	$Ir\ C_{73}H_{59}N_6$	1211.4395 (M+H)+	575	56	0.25	2
	AAA	$IrC_{69}H_{51}N_6$	1157.3917 (M+H)+	569	58	0.25	10
	ABC	$IrC_{71}H_{53}N_6$	1183.4076 (M+H)+	574	57	0.25	14
	AAC	$IrC_{69}H_{49}N_6$	1155.3771 (M+H)+	570	61	0.25	25
	BCC	$IrC_{71}H_{51}N_6$	1181.3921 (M+H)+	577	55	—	7
	ACC	$IrC_{69}H_{47}N_6$	1153.3613 (M+H)+	569	64	0.28	27
	CCC	$IrC_{69}H_{45}N_6$	1151.3442 (M+H)+	519	47	0.82	8
Library 2	EEE	$IrC_{93}H_{99}N_6$	1493.7676 (M+H)+	576	58	0.18	3
	EED	$IrC_{103}H_{103}N_6$	1617.7987 (M+H)+	576	60	0.16	12
	CEE	$IrC_{85}H_{81}N_6$	1379.6264 (M+H)+	575	61	0.19	11
	EDD	$IrC_{113}H_{107}N_6$	1741.8296 (M+H)+	575	59	0.19	14
	CED	$IrC_{95}\ H_{85}\ N_6$	1503.6566 (M+H)+	575	62	0.17	24
	CCE	$IrC_{77}H_{63}N_6$	1265.4846 (M+H)+	577	67	0.17	11
	CDD	$IrC_{105}H_{89}N_6$	1627.6853 (M+H)+	575	62	0.19	11
	CCD	$IrC_{87}H_{67}N_6$	1388.5133 (M+H)+	522	70	0.26	11
	CCC	$IrC_{69}H_{45}N_6$	1151.3435 (M+H)+	519	44	0.82	3
Library 3	KKK	$IrC_{57}H_{30}N_3F_{18}$	1292.1887 (M+H)+	507	52	0.74	12
	KKM	$IrC_{55}H_{32}N_3F_{12}$	1156.2156 (M+H)+	512	45	0.71	6
	KKL	$IrC_{61}H_{36}N_3F_{12}$	1232.2460 (M+H)+	512	44	0.82	30
	KMM	$IrC_{53}H_{34}N_3F_6$	1020.2376 (M+H)+	515	43	0.71	2
	KLM	$IrC_{59}H_{38}N_3F_6$	1096.2711 (M+H)+	516	47	0.62	11
	KLL	$IrC_{65}H_{42}N_3F_6$	1172.2998 (M+H)+	517	41	0.64	15
	MMM	$IrC_{51}H_{36}N_3$	884.2608 (M+H)+	519	41	0.77	1
	LMM	$IrC_{57}H_{40}N_3$	960.2931 (M+H)+	519	43	0.63	5
	LLM	$IrC_{63}H_{44}N_3$	1036.3240 (M+H)+	519	46	0.66	9
	LLL	$IrC_{69}H_{48}N_3$	1112.3546 (M+H)+	520	47	0.81	9
Library 4	NNN	$IrC_{54}H_{42}N_3$	926.3083 (M+H)+	520	46	0.85	7
	NNO	$IrC_{65}H_{49}N_4$	1079.3663 (M+H)+	522	45	0.77	6
	NOO	$IrC_{76}H_{56}N_5$	1232.4257 (M+H)+	522	49	0.77	15
	OOO	$IrC_{87}H_{63}N_6$	1385.4813 (M+H)+	525	45	0.71	35
	NNP	$IrC_{54}H_{39}N_4$	937.2922 (M+H)+	518	47	0.83	16
	NOP	$IrC_{65}H_{46}N_5$	1090.3481 (M+H)+	520	43	0.65	4
	OOP	$IrC_{76}H_{53}N_6$	1243.4054 (M+H)+	521	44	0.54	5
	NPP	$IrC_{54}H_{36}N_5$	948.2694 (M+H)+	515	44	0.76	11
	OPP	$IrC_{65}H_{43}N_6$	1101.3259 (M+H)+	517	44	—	1

[a]obtained via LC-MS (APCI); [b]determined relative to the standard quinine hemisulfate monohydrate; [c]estimated via the integral ratio of the products in the DAD trace.

phosphorescent blue emitter by spincoating layers of host material doped with a phosphorescent guest and examining the photoluminescence degradation under UV irradiation.[26] To gain a first hint on the stability of our compounds under continuous excitation, we examined the irradiation induced degradation of the complexes in solution. We found LEDs with an emission maximum of 400 nm to be the ideal light source as they allow the direct excitation of the MLCT absorption band and at the same time enable the irradiation through a chromatography glass vial. Toluene was chosen as the solvent for the photodegradation studies as it is a comparably inert and non coordinating solvent and is furthermore one of the preferred solvents

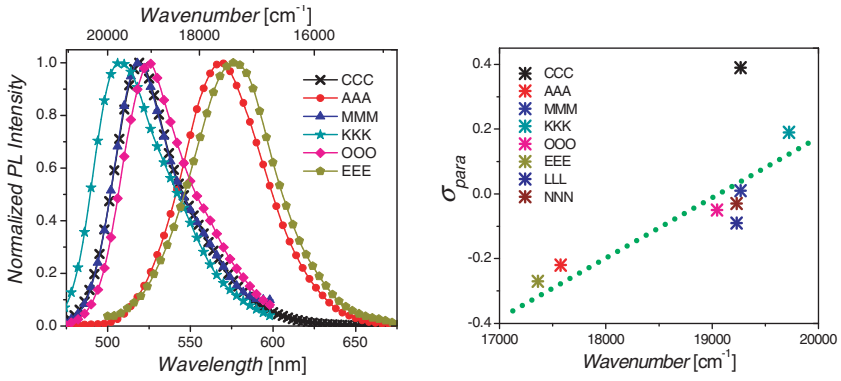


Figure 3. Phosphorescence spectra of selected homoleptic complexes illustrating the influence of electron donating and withdrawing groups on the emission energy (left). Hammett parameters σ_{para} plotted against the emission maxima (right). The dotted line is only a guide for the eye.

for solution processing of organic light-emitting devices. The irradiation was performed once under atmospheric and once under oxygen free conditions.[21]

$Ir(ppy)_3$ and similar compounds are known to be very effective sensitizers of singlet oxygen,[27] so we initially expected that the presence of those highly reactive oxygen species would lead to faster degradation under atmospheric conditions. When looking at the results of the photostabilities of the complexes we were surprised to find that for most compounds, the presence of oxygen in the solution seemed to increase the photostability instead.

A possible explanation for this unexpected observation could be that singlet oxygen is deactivated relatively fast in toluene. This implies that the observed degradation in toluene occurs mainly via the exited molecules themselves. Oxygen efficiently quenches the ^{3}MLCT excited state at near diffusion controlled rates, leading to much shorter exited state lifetimes and may thus reduce the probability of degradation via those states. A comparison of the homoleptic complexes showed that the overall trends in the photostability are similar under atmospheric and inert conditions. The fastest photodegradation could be observed for compounds **AAA** and **NNN** (**Figure 5**). The tris-phenyl substituted **MMM** showed a moderate photostability whereas the fully carbazole- and 3,5-*bis*(trifluoromethyl)phenyl- substituted complexes (**CCC** and **KKK** respectively) turned out to be the most stable of all screened compounds. Figure 5 (right) illustrates the influence of the different substituents on the degradation sensitivity for library 3. The presence of trifluoromethyl groups in the substituent (ligand **K**) seems to significantly increase the photostability of the complexes. This effect can be observed for compounds containing one to three bis(trifluoromethyl)phenyl groups under inert and atmospheric conditions alike.

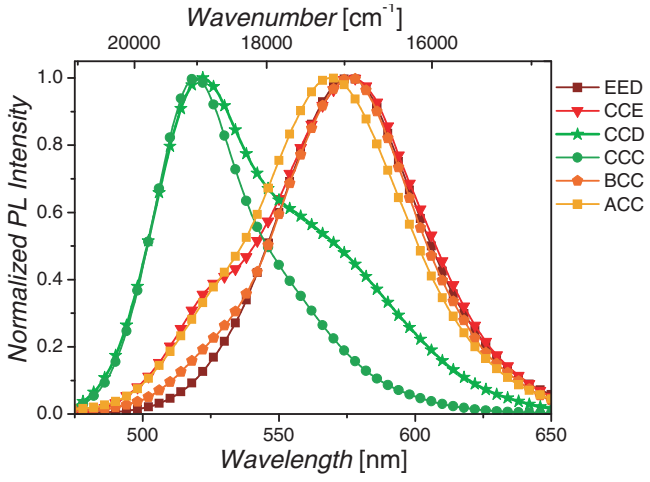


Figure 4. Phosphorescence spectra of compounds EED, CCE, CCD, CCC, BCC and ACC.

Further studies with a larger number of compounds will be necessary to establish structure-property relationships for the photostabilities in solution. More detailed investigations on the nature and products of the degradation pathways in solution as well as a comparison with device stabilities of selected emitters could shed light on the correlations and differences between the photo- and device-degradation of this class of compounds.

3. Conclusions

In conclusion we demonstrated that the described post modification strategy combined with a chromatographic separation and screening enables the rapid synthesis and characterization of potential new OLED emitters. We examined the photophysical properties of the compounds by obtaining absorption and emission spectra directly from the chromatographic separation. Trends in the dual emission behavior of selected heteroleptic complexes were observed that upon further studies might lead to the development of promising new compounds for white light emitting OLEDs. The determination of phosphorescence quantum yields in a separate experiment illustrated the antagonistic relationship between molecular flexibility and phosphorescence efficiency and helped to elucidate a promising new design principle for soluble and highly efficient phosphorescent emitters. By investigating the photodegradation of the libraries in solution, we found surprising trends and could identify compounds with increased stabilities compared to the rest of the libraries. Once a larger dataset will be available, a more detailed understanding of the degradation mechanisms and structure property relationships might help in the discovery of phosphorescent transition metal complexes with improved stabilities. The reported chromatography based screening of organo-transition metal complexes is not restricted to the development of new OLED emitters but may be easily applied for the accelerated discovery of materials for diverse other fields such as dyes for dye sensitized solar cells or new photoredox catalysts.

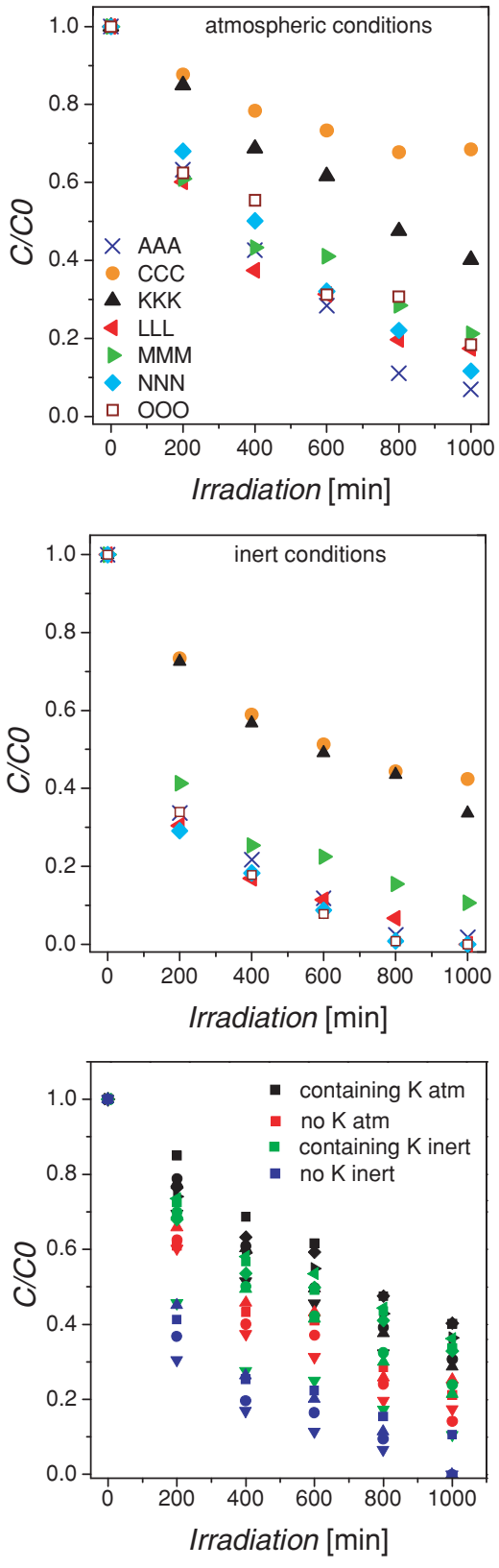


Figure 5. Photodegradation of the homoleptic complexes under atmospheric (left) and inert (center) conditions. Substitution effects on the photodegradation of library 3 (right).

4. Experimental Section

fac-Tris(5′-bromo-2-phenylpyridine)iridium was provided by Merck KGaA.[28] All solvents and other commercially available reagents were purchased from Alfa Aesar or Sigma Aldrich and were used as received without further purification. The solvents were used in p.a. quality and degassed via purging with nitrogen over 1 hour prior to use. For the chromatographic separation and analysis (sample preparation and mobile phase) we used LiChrosolv solvents, (DCM, THF and hexane) which were purchased from Merck KGaA.

General Procedure for the Combinatorial Buchwald-Hartwig Coupling: Tris(5′-bromo-2-phenylpyridine)iridium (0.1 mmol), an equimolar mixture of the secondary arylamines (0.4 mmol) and NaO^{t}Bu (0.8 mmol) were placed in a headspace vial. The vial was then flushed with nitrogen and sealed with a silicone/PTFE septum. Toluene (9 mL), 1,4-dioxane (5 mL) and 1 mL of catalyst solution (containing 0.03 mmol $Pd(OAc)_2$ and 0.18 mmol $P(^tBu)_3$ in degassed toluene) were added subsequently. The mixture was then stirred at 130 °C for 4 h in a custom made aluminum heating block. After the reaction mixture had cooled down to room temperature, the reaction mixture was washed with water and brine and dried over $MgSO_4$. The solvents were removed in vacuo to give an orange residue.

General Procedure for the Combinatorial Suzuki-Miyaura Coupling: Tris(5′-bromo-2-phenylpyridine)iridium (0.1 mmol), an equimolar mixture of the boronic acids (0.5 mmol) and K_3PO_4 (0.8 mmol) were combined in a headspace vial. The vial was then flushed with nitrogen and sealed with a silicone/PTFE septum. Degassed toluene, dioxane and water (5 mL each) and 1 mL catalyst solution (containing 0.03 mmol $Pd(OAc)_2$ and 0.18 mmol $P(o\text{-tolyl})_3$ in 10 mL degassed toluene) were added. The reaction mixture was stirred at 85 °C for 10 h in a custom made aluminum heating block. The toluene phase was washed with water and brine, dried over $MgSO_4$ and the solvent was removed in vacuo to give a yellow solid.

Synthesis of the Homoleptic Reference Complexes: The homoleptic reference complexes were synthesized as described for the combinatorial procedures but with only one amine or boronic acid respectively. The crude products were purified by recrystallization as specified with the characterization data.

Separation and Spectra: The semipreparative separation of the complex libraries was performed on an Agilent Technologies HPLC system consisting of a quaternary pump [G1311A], a vacuum degasser [G1322A], a thermostatted autosampler [G1329A], a thermostatted column compartment [G1316A], a diode-array detector (DAD) SL [G1315C] and a fluorescence detector (FLD) [G1321A] as well as an analytical scale fraction collector [G1364C]. The column used was a HIbar 250 mm × 10 mm × 5 µm diol column (Merck KGaA). The crude complex libraries were resolved in an appropriate volume of DCM (1–2 mL), filtered through a 2 µm PTFE syringe-filter and used for semipreparative HPLC separation using gradient elution (hexane/THF). All absorption and emission spectra were measured online via DAD and FLD detectors. The fractions were collected automatically (peak based fraction collection).

Identification: For the identification of the compounds, the collected samples were analyzed via LC-MS. The analysis was performed on an Agilent Technologies 1200 HPLC/MS system consisting of a binary pump SL [G1312B], a degasser [G1379B], an Infinity high performance micro autosampler [G1329B] with thermostat [G1330B], a thermostatted column compartment [G1316B], an Infinity diode-array detector (DAD) [G4212B] and an accurate mass Q-TOF/MS [G6530A] with an APCI (atmospheric pressure chemical ionization) ion source. The column used was a HIbar 250 mm × 4 mm × 5 µm diol column (Merck KGaA).

Quantum Yield Estimation: The PL quantum yields were determined relative to quinine hemisulfate monohydrate in 1 N H_2SO_4 (QY = 0.55). UV measurements were carried out on a Varian Cary 50Bio UV–vis spectrophotometer, phosphorescence measurements on a Varian Eclipse Fluorescence spectrophotometer in sealable Hellma precision cells [117.100F-QS] with silicone/PTFE coated septa. The complexes were dissolved in DCM and the solutions were degassed in the cells via vigorous argon purge through the solution prior to the measurements.

Photodegradation Studies: The pure complexes were dissolved in varying volumes of toluene (p.a.) to give solutions of similar concentration. The volume of toluene was adjusted according to the integration area of the peaks for each complex (from the semipreparative separation).

1 mL of the resulting solutions was transferred to a headspace vial and sealed with a silicone/PTFE septum. Two samples were prepared from each complex for the testing under atmospheric and inert conditions. In case of the photodegradation studies under inert conditions, the vials were degassed via 4 freeze-pump thaw cycles under argon. All samples were irradiated in a custom made irradiation unit (SIM GmbH, picture see supporting information). It consists of an aluminum printed circuit board with 30 400 nm LEDs, connected to a cooling unit, that ensures a constant temperature of 13 °C of the board during the irradiation. Two 15 sample chromatography trays can be placed in the unit so that each of the sample vials is centered over one LED (d = 1 cm). The total duration of irradiation was 1000 min. After 0, 200, 400, 600, 800 and 1000 min, the samples were analyzed via HPLC (analytical system, see above). The percentage of remaining emitter was determined via the integration of the DAD signal at 305 nm in relation to that of an external standard (quaterphenyl in toluene, 0.026 mM).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.H. and S.S. contributed equally to this work. The authors would like to thank Sabine Reuke (Merck KGaA) for help with the chromatography conditions. The authors gratefully acknowledge financial support by the German Federal Ministry of Education and Research (BMBF) and Deutsche Forschungsgemeinschaft (GRK 1626, chemical photocatalysis).

Received: February 8, 2012
Revised: March 15, 2012
Published online: May 8, 2012

[1] a) K. K.-W. Lo, C.-K. Chung, T. K.-M. Lee, L.-H. Lui, K. H.-K. Tsang, N. Zhu, *Inorg. Chem.* **2003**, *42*, 6886; b) K. K.-W. Lo, D. C.-M. Ng, C.-K. Chung, *Organometallics* **2001**, *20*, 4999; c) K. K.-W. Lo, K. Y. Zhang, S.-K. Leung, M.-C. Tang, *Angew. Chem. Int. Ed.* **2008**, *47*, 2213.

[2] a) C. S. K. Mak, D. Pentlehner, M. Stich, O. S. Wolfbeis, W. K. Chan, H. Yersin, *Chem. Mater.* **2009**, *21*, 2173; b) Y. You, S. Y. Park, *Adv. Mater.* **2008**, *20*, 3820.

[3] a) W. Zhao, F. N. Castellano, *J. Phys. Chem. A* **2006**, *110*, 11440; b) T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560.

[4] E. Baranoff, J.-H. Yum, M. Graetzel, M. K. Nazeeruddin, *J. Organomet. Chem.* **2009**, *694*, 2661.

[5] a) B. F. DiSalle, S. Bernhard, *J. Am. Chem. Soc.* **2011**, *133*, 11819; b) J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502; c) N. Sutin, C. Creutz, E. Fujita, *Comments Inorg. Chem.* **1997**, *19*, 67; d) Y.-J. Yuan, Z.-T. Yu, X.-Y. Chen, J.-Y. Zhang, Z.-G. Zou, *Chem. –Eur. J.* **2011**, *17*, 12891.

[6] a) K. Zeitler, *Angew. Chem., Int. Ed.* **2009**, *48*, 9785; b) H.-W. Shih, M. N. Vander Wal, R. L. Grange, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2010**, *132*, 13600; c) A. G. Condie, J. C. González-Gómez, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2010**, *132*, 1464.

[7] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151.

[8] a) T. Hofbeck, H. Yersin, *Inorganic Chemistry* **2010**, *49*, 9290; b) H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck, T. Fischer, *Coord. Chem. Rev.* **2011**, *255*, 2622.

[9] a) Y. You, S. Y. Park, *Dalton Trans.* **2009**, 1267; b) Y. Chi, P.-T. Chou, *Chem. Soc. Rev.* **2010**, *39*, 638; c) P. T. Chou, Y. Chi, *Chem. –Eur. J.* **2007**, *13*, 380.

[10] a) E. Baranoff, S. Fantacci, F. De Angelis, X. Zhang, R. Scopelliti, M. Grätzel, M. K. Nazeeruddin, *Inorg. Chem.* **2010**, *50*, 451; b) F. De Angelis, S. Fantacci, N. Evans, C. Klein, S. M. Zakeeruddin, J.-E. Moser, K. Kalyanasundaram, H. J. Bolink, M. Grätzel, M. K. Nazeeruddin, *Inorg. Chem.* **2007**, *46*, 5989; c) C. L. Ho, W. Y. Wong, Z. Q. Gao, C. H. Chen, K. W. Cheah, B. Yao, Z. Y. Xie, Q. Wang, D. G. Ma, L. X. Wang, X. M. Yu, H. S. Kwok, Z. Y. Lin, *Adv. Funct. Mater.* **2008**, *18*, 319; d) J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 1713; e) M. S. Lowry, W. R. Hudson, R. A. Pascal, S. Bernhard, *J. Am. Chem. Soc.* **2004**, *126*, 14129.

[11] E. M. Gordon, R. W. Barrett, W. J. Dower, S. P. A. Fodor, M. A. Gallop, *J. Med. Chem.* **1994**, *37*, 1385.

[12] C. Gennari, U. Piarulli, *Chem. Rev.* **2003**, *103*, 3071.

[13] N.-M. Hsu, W.-R. Li, *Angew. Chem., Int. Ed.* **2006**, *45*, 4138.

[14] E. Baranoff, I. Jung, R. Scopelliti, E. Solari, M. Grätzel, M. K. Nazeeruddin, *Dalton Trans.* **2011**, *40*, 6860.

[15] a) C. E. Kibbey, *Lab. Rob. Autom.* **1997**, *9*, 309; b) L. Zeng, L. Burton, K. Yung, B. Shushan, D. B. Kassel, *J. Chromatogr., A* **1998**, *794*, 3; c) H. N. Weller, *Mol. Diversity* **1998**, *4*, 47.

[16] a) C. Adachi, M. A. Baldo, S. R. Forrest, M. E. Thompson, *Appl. Phys. Lett.* **2000**, *77*, 904; b) Y. Kawamura, K. Goushi, J. Brooks, J. J. Brown, H. Sasabe, C. Adachi, *Appl. Phys. Lett.* **2005**, *86*, 071104.

[17] D. Tanaka, H. Sasabe, Y.-J. Li, S.-J. Su, T. Takeda, J. Kido, *Jpn. J. Appl. Phys.* **2007**, *46*, L10.

[18] a) N. Cumpstey, R. N. Bera, P. L. Burn, I. D. W. Samuel, *Macromolecules* **2005**, *38*, 9564; b) Y. You, C.-G. An, J.-J. Kim, S. Y. Park, *J. Org. Chem.* **2007**, *72*, 6241; c) Y. You, C.-G. An, D.-S. Lee, J.-J. Kim, S. Y. Park, *J. Mater. Chem.* **2006**, *16*, 4706.

[19] P. Stoessel, H. Spreitzer, H. Becker, *Rhodium and Iridium Complexes, WO02068435A1*, *Covion Organic Semiconductors*, **2002**.

[20] a) P. Stoessel, I. Bach, H. Spreitzer, *Rhodium and Iridium Complexes, WO200402 6886A2*, *Covion Organic Semiconductors*, **2004**; b) P. Stoessel, H. Spreitzer, H. Becker, *Rhodium and Iridium Complexes WO02081488A1*, *Covion Organic Semiconductors*, **2002**; c) R. M. Anemian, B. Schroeder, A. H. Parham, C. d. Nonancourt, *Metal Complexes, WO2011141120A1*, *Merck Patent GmbH*, **2011**.

[21] The solutions were degassed via 4 consecutive freeze-pump-thaw cycles applying a membrane vacuum pump (~10 mbar) and back-filling with argon. It should be noted that a complete, quantitative removal of oxygen is unlikely under these conditions but it should be sufficient to establish the overall trend of the influence of oxygen on the photostability of the materials.

[22] K. Ono, M. Joho, K. Saito, M. Tomura, Y. Matsushita, S. Naka, H. Okada, H. Onnagawa, *Eur. J. Inorg. Chem.* **2006**, *2006*, 3676.

[23] Y. You, K. S. Kim, T. K. Ahn, D. Kim, S. Y. Park, *J. Phys. Chem. C* **2007**, *111*, 4052.

[24] a) N. C. Giebink, B. W. D'Andrade, M. S. Weaver, J. J. Brown, S. R. Forrest, *J. Appl. Phys.* **2009**, *105*, 124514; b) N. C. Giebink, B. W. D'Andrade, M. S. Weaver, P. B. Mackenzie, J. J. Brown, M. E. Thompson, S. R. Forrest, *J. Appl. Phys.* **2008**, *103*, 044509; c) R. Seifert, S. Scholz, B. Lussem, K. Leo, *Appl. Phys. Lett.* **2010**, *97*, 013308.

[25] a) T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard, M. E. Thompson, *J. Am. Chem. Soc.* **2009**, *131*, 9813; b) I. R. d. Moraes, S. Scholz, B. Lüssem, K. Leo, *Org. Electron.* **2011**, *12*, 341.

[26] W. Sotoyama, T. Satoh, M. Kinoshita, M. Tobise, K. Kawato, T. Ise, H. Takizawa, S. Yamashita, *Fujifilm Research and Development* **2010**, No.*055*, 24.

[27] a) R. Gao, D. G. Ho, B. Hernandez, M. Selke, D. Murphy, P. I. Djurovich, M. E. Thompson, *J. Am. Chem. Soc.* **2002**, *124*, 14828; b) S.-y. Takizawa, R. Aboshi, S. Murata, *Photochem. Photobiol. Sci.* **2011**, *10*, 895; c) P. I. Djurovich, D. Murphy, M. E. Thompson, B. Hernandez, R. Gao, P. L. Hunt, M. Selke, *Dalton Trans.* **2007**, 3763.

[28] P. Stoessel, H. Spreitzer, H. Becker, Method for the Production of Highly Pure, Tris-ortho Metalated Organo-Iridium Compounds, WO02060910A1, **2002**.