

Positively Charged Iridium(III) Triazole Derivatives as Blue Emitters for Light-Emitting Electrochemical Cells

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Cationic blue-emitting complexes with (2,4-difluoro)phenylpyridine and different 1,2,3-triazole ligands are synthesized with different counterions. The influence of the substituents on the triazole ligand is investigated as well as the influence of the counterions. The substituents do not change the emission energy but, in some cases, slightly modify the excited-state lifetimes and the emission quantum yields. The excited-state lifetimes, in apolar solvents, are slightly dependent on the nature of the counterion. A crystal structure of one of the compounds confirms the geometry and symmetry postulated on the basis of the other spectroscopic data. Light-emitting electrochemical cell devices are prepared and the recorded emission is the bluest with the fastest response time ever reported for iridium complexes.

1. Introduction

Light-emitting electrochemical cells (LEECs) represent an interesting possible alternative to the more-investigated organic lightemitting diodes (OLEDs). The difference between OLEDs and LEECs resides on the use of charged complexes that provide the ionic transport in the device. In other words, the mobile ions in the layer move towards the electrodes upon application of a voltage, and this migration causes a drop of potential at the electrodes and, as a result, charge injection becomes easier and will take place when the applied voltage exceeds the potential corresponding to the bandgap of the electroluminescent material.^[1-6] Therefore, no additional layers are needed in the device and the emissive layer can be solution processed, which makes industrial manufacturing easier. The LEEC devices also have other advantages such as that the electrodes of LEECs can be made of cheaper and less reactive materials than in OLEDs, since the work functions have no influence on the charge injection. Furthermore, the applied voltage does not drop over the bulk film but only within the thin ionic

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 double layers. As a result, fabrication of thick luminescent devices without affecting their efficiencies is possible, as well as the preparation of large surface LEECs.

The first OLEEC was reported by Pei et al. and consists of a polymer where a salt was added to have mobile ions.^[3] Instead of using additional salts in the emissive layer, the emitters can be salts themselves. The first LEEC based on a cationic transition metal complex was reported in 1996 by Rubner et al.^[1] In 2004, we reported a LEEC based on a dinuclear ruthenium complex as dopant of a polymer, exhibiting a two-color behavior.^[7] At the moment, the most complexes based osmium,^[27] platinum,^[28,29] and even copper.^[30,31] Even positively

osmium,^[27] platinum,^[28,29] and even copper.^[30,31] Even positively charged polymers made from zinc-terpyridine complexes have been prepared showing electroluminescence.^[32] The most common counterion is hexafluorophosphate because complexes can be easily precipitated and purified with this anion. Other studied counterions include chloride, perchlorate, and tetrafluoroborate.^[31]

A drawback of LEECs is that usually the turn-on time, the time needed to see the emission after the application of the voltage, is very long (minutes or hours) due to the slow diffusion of charges that results in the formation of the double-layers. This prevents their use in display applications but LEECs are still very appealing for lighting devices where large-area emission and cheap and easy processing are required. In order to decrease the turn-on time of LEEC devices ionic liquids have been employed to replace the more common polymeric matrices used to process the emissive layer.^[21,25,33] In fact, ionic liquids allow good film formation, since most of the charged species are soluble in these solutions and they increase the amount of mobile ions inside the layer, especially since the cations of the ionic liquids show a higher mobility than the relatively bulky monocationic complexes. On the other hand, the use of bulky charged complexes avoids concentration quenching inside the device by increasing the distance between the emissive complexes.^[9,34]

In this paper, we report the synthesis, characterization, and photophysical and electrochemical properties of a series of monocationic iridium complexes bearing two difluorophenylpyridine (dfppy) ligands and a pyridine-N-substituted-1,2,3-triazole. One of the complexes has also been crystallized to show the general structure and geometry of the complexes and the X-ray data are also





discussed. The use of triazole ligands already explored by our group for OLED technology has the advantage of an easy transformation of neutral complexes into charged ones by substitution on the N3-atom of the triazole moiety.^[35] Furthermore, the LUMO of this ligand is higher in energy than the LUMO of the more widely used bipyridine and phenanthroline ligands, maintaining the high-energy emission of the triazole complexes, which falls into the blue region of the visible spectrum.^[9,11,36–44] We demonstrate that these charged complexes are blue emitters, also in electroluminescent devices, and can be used as an electroluminescent layer in combination with ionic liquids in LEEC devices. We also compare the influence of the substituent and the counterions on the photophysical properties as well as on device characteristics. To the best of our knowledge, the complexes reported in this paper are the bluest electroluminescent compounds, with the fastest turn on time ever reported. A similar emission energy was observed for a different class of iridium complexes.^[10]

2. Results and Discussion

2.1. Synthesis and Characterization

Scheme 1 represents a general synthetic route to prepare the ligands that will be then used for complexation as shown in Scheme 2. The 1,2,3-triazoles were prepared by click chemistry,^[45,46] that is, copper-catalyzed Huisgen cycloadditions. 2-Ethynylpyridine was reacted with a substituted azide under the conditions given in Scheme 2 to give the desired product in one step. The synthesis of the previously reported triazole **1**



Scheme 1. 1,2,3-triazole ligands and appropriate click conditions for the different ligands.

was the only one that had to be carried out under anhydrous conditions, following a new synthetic route.^[47,48] After the reaction, aqueous ammonia solution (32%) was added to the reaction mixture and stirred for 1 h in order to remove the catalyst forming the characteristic blue water-soluble tetraamminediaquacopper(II) complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$. Then diethyl ether was added, and the aqueous layer was separated. The organic layer was washed with water until the washings reached pH 7.

To form the final complex, the triazoles and the dichloro-bridged iridium complex were stirred together in a dichloromethane/ ethanol mixture (3:1) overnight.^[46,49] The complexes were purified by repeated recrystallization. They have been characterized using ¹H NMR and ¹⁹F NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. Additionally, a crystal structure of complex **8a** was obtained in order to illucidate the structure. Synthetic details and the full characterization can be found later.

2.1.1. Crystal Structure of Complex 8a

The crystal structure depicted in the Supporting Information, S1 shows that the nitrogen atoms of the two dfppy ligands are trans to each other with Ir–N bond lengths of 2.056 and 2.048 Å, respectively. The Ir–C bond lengths of the cyclometalating carbon atoms on these ligands are 2.017 and 2.011 Å, respectively. The longest bond lengths to Ir are from the nitrogen atoms on the triazole ligand from the pyridine moiety with a distance of 2.179 and 2.128 Å from the triazole moiety. The torsion angle between the triazole and the first phenyl ring is 27.74° and the torsion angle between the phenyl rings of the biphenyl part is -15.01°.

2.2. Photophysical Characterization

2.2.1. Absorption and Emission Spectroscopy

The absorption spectra of the complexes 5-8 were recorded in dichloromethane solutions at room temperature (Fig. 1 for 5a-8a, Supporting Information, S2 for 5b-8b and 4). The absorption bands at high energy (240-320 nm) can be assigned to $\pi \rightarrow \pi^*$ transitions involving the coordinated ligands. In particular, the main peak at \sim 250 nm are transitions localized on the dfppy ligands and on the triazole moiety, while at lower energy (300-320 nm) the pyridine moieties of the ligands are the major players. The weaker absorption bands (320-450 nm) are assigned to spin-allowed singlet-to-singlet metal-to-ligand charge-transfer (¹MLCT) and at lower energies to spin-forbidden singlet-totriplet metal-to-ligand charge-transfer (³MLCT) transitions. These last bands are quite intense despite the forbidden character. This is due to the heavy metal atom effect, which causes a strong spin-orbit coupling.^[50]

It is interesting to notice that the absorption spectra of the biphenyl derivative compounds







Scheme 2. General route for the preparation of the iridium complexes presented in this paper including the studied counterions and the abbreviations used.

8a and **8b** show another band with high intensity at 290 nm (see Supporting Information, S2). This band is due to $\pi \rightarrow \pi^*$ transitions on the biphenyl substituent on the triazole ligand, which can be confirmed by the absorption spectrum of the free ligand, which shows a similar band at 294 nm.

All the investigated complexes show bright blue emission at room temperature in solution. They are almost identical despite the different substitution on the triazole ligand. The photoluminescence (PL) spectra for complexes **5a** and **7a**, **6a** and **8a**, and **5–8b** in degassed dichloromethane solution are found in Figure 2 and in the Supporting Information, S3a and S3b. They have similar structured features with an intense band at 452 nm, a second less intense vibronic progression at 483 nm and a shoulder around 505 nm. The structured emission spectrum is due to a large amount of ligand-centered (^{3}LC) character of the excited state, which is indeed a mixture between $^{3}MLCT$ and ^{3}LC states. $^{[17,51-53]}$

To the best of our knowledge these complexes are amongst the bluest charged iridium complexes ever reported.^[8,10,54] Their emission quantum yields are remarkably high for charged complexes in solution and for all the complexes, yields are around 25%, except for complex 8, in degassed solution. The emission quantum yields dramatically decrease in aerated solution due to





Figure 1. Absorption spectra of complexes 5a (-), 6a (...), 7a (- - -), and 8a (- - -) in CH_2Cl_2 solutions at room temperature.



1814

Figure 2. Normalized RT emission spectra of the complexes 5a (-) and 7a (- -) in deaerated solutions in dichloromethane excited at 352 nm.

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the quenching by oxygen, confirming the triplet character of the emission. Complexes **8a** and **8b** show emission quantum yields around 10%.

The excited-state lifetimes are somewhat dependent on the counterion present in the complex. We believe that in dichloromethane, where the ions are very close to each other, the different counterions could be responsible for a slightly different packing between the cationic and the anionic part. To confirm this hypothesis the lifetimes of the complexes 6a and 6b were investigated also in a polar solvent (acetonitrile), where the ions should be solvated and separated. The data show almost identical lifetimes of 1.69 and 1.65 µs, respectively, for the two different counterions. We also compared the absorption and emission spectra of **6b** in the two solvents (see Supporting Information, S8), but no appreciable changes were detected. The excited-state lifetimes of the complexes are rather short, below 1 µs, (see Table 1) for iridium complexes and are very similar for all the complexes with the exception of the complexes bearing the biphenyl substituent on the triazole.

For these, the lifetimes are almost four times higher, which is an apparent contradiction for these complexes. When the biphenyl is present on the triazole the lowest excited state should be lower in energy than the ligand with saturated group as substituent. Furthermore, the higher conjugation, triazole and two phenyls, lower the triplet excited state of the ligand, allowing a stronger mixing between the with the ³MLCT states. Therefore we believe that in the case of the complexes 8a and 8b the lowest excited state involves the substituted triazole ligand and has a stronger ³LC character than for the other complexes, due to a larger mixing (closer energy) of the ligand-centered states with the ³MLCT states. This different, more ligand-centered character would explain the longer excited-state lifetimes on one hand, and the lower quantum yields on the other hand (Table 1). Furthermore, the free rotation of the phenyl rings in the excited state would influence the nonradiative decay rates, therefore reducing the emission quantum yields. These non-radiative contributions can be calculated through the radiative and non-radiative rate constants (see Supporting Information, S6), which indeed show lower radiative rate constants for complexes 8a and 8b.^[53]

2.3. Electrochemical Characterization

In order to investigate the frontier orbitals of the compounds, cyclic voltammetry (CV) was performed in freshly distilled acetonitrile

solutions. The compounds show oxidations in the range of +1.19 to +1.27 V. Compounds 6a and 6b only show semireversible oxidations. Compared to neutral Ir complexes with two dfppy ligands and a pyridine-1,2,4-triazole ligand with oxidations at around +0.96 V the oxidations occur at higher potential due to the absence of the negative charge on the nitrogen of the triazole ligand, resulting in a much weaker sigma-donation, which makes the iridium ion more positive than in neutral complexes.^[35] This causes a more difficult oxidation of the metal, which is less electron rich, and an increase in the oxidation potential is observed. The first reductions of the complexes are not fully reversible and can be assigned to a reduction of the pyridine rings on the ancillary ligands. Values in the same range have been reported for complexes containing phenylpyridines and pyridine-pyrazoles or bipyridines as ancillary ligands.^[10,37,40,41,44] The second reductions, which are around -2.5 V, are assigned to the fluorinated phenylpyridines. Representative waves of the measurements can be seen in the Supporting Information, S4.

2.4. Device Properties

2.4.1. Fabrication of LEEC Devices

All LEEC devices incorporating the triazole-based complex materials were fabricated by spin-coating on indium tin oxide (ITO)-covered glass substrates. The typical layer structure sketched in the schematic view of Figure 3 consists of 100 nm poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and 70 nm of emitting layer composed of the chosen iridium complex blended with an ionic liquid tetrabutylammonium trifluoromethanesulfonate (TBAOTf), which accelerates the charge injection into the emitting layer and hence reduces the turn-on time of the device. The reduction of turn-on times in LEECs using ionic liquids like 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM⁺PF₆⁻) was already shown by Malliaras et al.^[55] After depositing the PEDOT:PSS layer, the emitting layer was prepared: 10 mg transition metal complex material together with ionic liquid were diluted in 1 mL acetonitrile in a mole ratio 1:1. The solution was filtered using a 0.1 µm PTFEfilter, spin-coated on top of the PEDOT: PSS layer, and the resulting film was baked for 2 h at 80 °C under vacuum. Finally, a 150-200 nm thick aluminum layer was evaporated on top used as a

Table 1. Absorption and emission spectra, quantum yield, lifetime and redox potentials of complexes 5a-8b [a].

Complex	$\lambda_{\rm max,abs}$ [b][nm] (ϵ \times 10 ⁴ μ^{-1} cm ⁻¹)	$\lambda_{\max,em}$ [c][nm]	τ [µs] deaer.	$\Phi_{\rm em}$ deaer.[d]	$E^{1/2}1/2_{Ox}$ [V]	$E^{1}/_{2^{\text{Red}}}$ [V]
5a	248(5.13), 302(2.14,sh), 362(5.50)	453(1), 483 (0.87)	0.68	0.21	1.22[f]	-2.18[f], -2.59[f]
5b	248(5.24), 303(2.03,sh), 363 (5.89)	453(1), 483 (0.87)	0.58	0.21	1.24[f]	-2.16[f], -2.59[f]
6a	247(4.99), 302(1.90,sh), 363(5.49)	452(1), 483 (0.87)	0.73	0.15	1.27[e]	-2.17[f], -2.51 [f]
6b	247(5.27), 303(1.97,sh), 363(5.63)	452 (1), 483 (0.87)	0.63	0.22	1.25[e]	-2.14[f], -2.57 [f]
7a	259(7.73), 304(3.29,sh), 362(8.73)	453(1), 483(0.93)	0.87	0.24	1.19[e]	-2.02[f], -2.44[e]
7b	259(8.34), 314(3.44,sh), 362(7.97)	453(1), 483(0.94)	0.72	0.17	1.22[e]	-2.01[f], -2.42[e]
8a	261(3.89), 291(3.85), 314(2.71,sh), 358(6.13)	452 (1), 482 (0.88)	2.24	0.11	1.26[e]	-2.08[f], -2.52[f]
8b	262(4.76), 290(4.73), 314(3.32,sh), 360(7.48)	452 (1), 482 (0.87)	2.05	0.09	1.25[e]	-2.07[f], -2.52[f]

[a] All data for complexes in dichloromethane. [b] "sh" denotes a shoulder. [c] $\lambda_{exc} = 350$ nm. [d] Quantum yields were measured in an integrating sphere system. [e] Irreversible. [f] Not fully reversible.









Figure 3. Schematic view of the device structure.

70nm Emitting Layer 100nm PEDOT:PSS

Table 2. Summary of the device characteristics.

Complex	t _{max} [a] [s]	$L_{max}[b] [cd m^{-2}]$	$\lambda_{\max, EL}[c]$ [nm]	Lifetime [d] [min]
5a	390	14.5	460, 488	38.0
5b	240	19.4	460, 488	10.5
6a	860	44.9	460, 488	24.5
6b	120	31.4	456, 488	3.4
7a	180	42.7	460, 488	10.0
8b	310	32.1	456, 488	28.6

[a] Time required to reach the maximum luminance. [b] Maximum luminance value for a constant bias voltage 5.0V applied to the device. [c] Wavelength peak measured in electroluminescence at 5.5 V. [d] Time to reach the half of the maximum luminance under a constant bias voltage 5.0 V.

In Figure 5 the electroluminescent spectra for the complexes 5a and 5b measured at a fixed voltage (5.5 V) are shown. As can be seen

the devices exhibited blue electroluminescence with a first

emission maximum at a wavelength of 456-460 nm and a second

maximum at 488 nm. This characteristic double peak emission

was also observed for the complexes 6-8 having a first peak at 456-

460 nm and a second peak at 488 nm. Hence, as observed in case of

the PL spectra in degassed dichloromethane solution, all LEEC

devices show almost identical emission maxima independent of the counterions (Fig. 5). We have also compared the electroluminescent spectra with the solid-state spectra of the complexes

recorded both in ionic liquid and in a poly(methyl methacrylate)

(PMMA) matrix. The results (Supporting Information, S7a and b)

demonstrate that the matrix has a negligible influence on the

emission properties. In the electroluminescence spectra the two

spectral peaks are slightly shifted towards higher wavelength

values compared to the PL data from 452 to 456-460 nm and from

482 to 488 nm. Such wavelength shifting phenomena for blue-

emitting iridium LEECs have also been reported in recent

papers.^[41] It has to be considered that the spectral shift is very small

for a device using ionic liquids. For recently reported good blue

LEEC devices the use of ionic liquids made the EL spectrum shift

66 nm to the red.^[10]

cathode, and the device was encapsulated by a glass capping layer to protect the organic layers against penetrating oxygen and water. The active lighting area was 4 mm^2 .

2.4.2. Electroluminescent Properties of LEECs

As an example in Figure 4 the corresponding results for the timedependent luminance (L) and current (C) of the triazol-based iridium complexes 5a and 5b are presented. The L(t) and C(t)characteristics are based on averaged data of up to 6 single devices for each complex. For a description of the light measurements please refer to the experimental part. For the shown complex, the maximum luminance exhibits a comparable magnitude for both types of counterions with 19.4 cd m^{-2} for the devices with PF₆ counterions (**5b**) and 14.5 cd m^{-2} for the devices with BF₄ counterions (5a). However, the lifetime (time to reach the half of the maximum luminance) is higher for the latter one (38.0 min for **5a** and 10.5 min for **5b**). Averaged data for t_{max} (time required to reach the maximum luminance), L_{max} (maximum luminance), and lifetime for complexes 5a, 5b, 6a, 6b, 7a, and 8b are depicted in Table 2. For the investigated set of complexes, t_{max} ranges between 120 (6b) and 860 s (6a), $L_{\rm max}$ between 14.5 (5a) and 44.9 cd m⁻² (6a) and the lifetime between 3.4 (6a) and 38 min (5a). The short time scale for t_{max} in the range of seconds is facilitated by the TBAOTf ionic-liquid blend. The observed differences in the device performance of the complexes, further device optimizations with regard to brightness, and lifetime, as well as the role of the counterions, are currently still under investigation and out of the scope of this work.



Figure 4. LEEC device L and C measured at fixed voltage (5.0 V) as a function of time for the complexes 5a (-) and 5b (...).



Figure 5. Electroluminescent spectra and pictures of LEEC devices biased at 5.5 V based on complexes 5a (-) and 5b (...).

1816

Lum / cd m⁻²



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3. Conclusions

We have reported a series of phosphorescent cationic iridium(III) complexes based on N-substituted pyridine-1,2,3-triazoles. The complexes were synthesized in reasonable yields and fully characterized. They show blue PL and electroluminescence. The turn-on times of the devices are in the range of seconds and show only small spectral shifts despite the use of ionic liquids. To our knowledge these are the bluest LEEC devices reported showing such fast device-response times.

4. Experimental

Photophysics: Absorption spectra were measured on a Varian Cary 5000 double-beam UV-Vis-NIR spectrometer and baseline corrected. Steadystate emission spectra were recorded on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon-arc lamp, doublegrating excitation and emission monochromators $(2.1 \text{ nm mm}^{-1} \text{ disper-}$ sion; 1200 grooves mm⁻¹), and a Hamamatsu R928 photomultiplier tube or a TBX-4-X single-photon-counting detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) by standard correction curves. Time-resolved measurements were performed using the time-correlated single-photon-counting (TCSPC) option on the Fluorolog 3. NanoLED (402 nm; FHWM < 750 ps) with repetition rates between 10 kHz and 1 MHz used to excite the sample. The excitation sources were mounted directly on the sample chamber at 90° to a doublegrating emission monochromator (2.1 nm mm⁻¹ dispersion; 1200 grooves mm^{-1}) and collected by a TBX-4-X single-photon-counting detector. The photons collected at the detector are correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected using an IBH Data Station Hub photon counting module and data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). The quality of the fit was assessed by minimizing the reduced chi squared function (χ^2) and visual inspection of the weighted residuals.

Luminescence quantum yields were measured with a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source (150 W), monochromator, C7473 photonic multi-channel analyzer, integrating sphere, and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan).

All solvents were spectrometric grade. Deaerated samples were prepared by the freeze-pump-thaw technique.

Cyclic Voltammetry: CV was performed in a gas-tight single-compartment three-electrode cell using a Voltalab 40 system from Radiometer Analytical that consists of a PGZ301 potentiostat and Voltamaster 4 software. The working electrode is a Pt disc, the counter electrode a Pt wire, and an Ag wire was used as a pseudoreference electrode. CVs were elucidated and compared using IGOR. All glassware was dried prior to use. The compounds (electrolyte, analyte, and reference) were placed in a Schlenk flask that was then evacuated and heated with a heat gun to eliminate any moisture and oxygen that had entered during addition [56]. The flask was then evacuated and filled three times with dry N₂. The solvent was added via syringe directly to the sealed Schlenk flask, the solution sonicated if necessary and then degassed for 10 min with a gentle stream of dry N_{2} [57]. After degassing, the solution was added, via syringe, to the electrochemical cell under a positive N2 pressure. The solution was kept under a positive N₂ pressure during the measurements (see Supporting Information, S3).

Device Preparation: PEDOT:PSS (Clevios AI4083) was supplied by H. C. Starck and TBAOTf from Sigma Aldrich. In order to investigate the electroluminescent properties of the LEEC devices the luminance was detected as a function of time at an applied bias voltage of 5 V (constant voltage mode). All electro-optical measurements were powered by using a power source meter E3646A from Agilent Technologies. The resulting light output was detected by calibrated photo diodes. The induced currents

through the device and through the photodiodes were measured by current meters from National Instruments (NI9219). The maximal allowed current through the devices was limited to 40 mA (current compliance). Using a spectral camera (PR650) the photodiodes were calibrated and the electroluminescent spectra of the different LEEC devices were detected in the visible range between 380 and 780 nm.

X-ray Crystallography: Data sets were collected with a Nonius KappaCCD diffractometer equipped with a rotating anode generator. Programs used were as follows: data collection COLLECT [58], data reduction Denzo-SMN [59], absorption correction SORTAV [60,61] and Denzo [62], structure solution SHELXS-97 [63], structure refinement SHELXL-97 [64], and graphics SCHAKAL [65].

Synthesis and Characterization: All reagents were analytical grade and used as received. Solvents were purified according to the standard procedures [66]. All reactions were performed under inert atmosphere (Schlenk-line techniques), except where noted. Column chromatography (CC) was performed with silica gel 60 (particle size $63-200 \,\mu\text{m}$, 230-400 mesh, Merck) using common flash procedures [67]. NMR spectra were recorded on an ARX 300 or an AMX 400 from Bruker Analytische Messtechnik (Karlsruhe, Germany). The ¹H NMR chemical shifts (δ) of the signals are given in ppm and referenced to residual protons in the deuterated solvents: chloroform-d₁ (7.26 ppm), dimethyl sulfoxide-d₆ (2.50 ppm), or acetone-d₆ (2.09 ppm). The $^{19}{\rm F}$ NMR chemical shifts are referenced to CFCl₃ (0.00 ppm) as an internal standard. The signal splittings are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants (J) are given in Hertz (Hz). Mass spectrometry was performed in the Department of Chemistry, University of Münster. Electrospray ionization (ESI) mass spectra were recorded on a Bruker Daltonics (Bremen, Germany) MicroTof with loop injection. Elemental analysis was recorded at the University of Milan, Italy.

2-(2,4-difluorophenyl)pyridine and (F2ppy)2Ir(µ-Cl)2Ir(F2ppy)2 were prepared as previously reported [49]. The 1,2,3-triazole based ligands were prepared by copper(I)-catalyzed click chemistry. Ligands 1 and 2 (Scheme 1) have been reported before with different synthetic routes [47,68-71]. For ligand 1 we report a new procedure, and the route used for ligand 2 was taken from a similar compound with a phenyl ring instead of the pyridine [72]. The triazole 2 could be easily synthesized in a dichloromethane/ethanol mixture (4:1) in the presence of [Cu(MeCN)₄]PF₆ and precipitated from the reaction mixture. Washing with dichloromethane/ethanol and filtration through silica gave a pure product. Ligand 3 was synthesized by a one-pot reaction starting from aniline. The azide necessary for the reaction was generated in situ with tert-butylnitrite and azidotrimethylsilane, followed by a classical click reaction [73]. Triazole 4 was obtained using the classical click chemistry conditions, with copper(II)sulfate and sodium ascorbate to generate the catalytic Cu(I) in situ. The work-up was similar to the one of 1. It turned out to be very helpful to stir the reaction mixtures with 32% ammonia solution for 30 min before starting the work-up. Since the pyridine-triazoles are capable of binding to copper the reaction yield was lowered strongly because of the formation of copper complexes with the product. The presence of copper can be monitored easily by the color of the ammonia solution because it turns blue due to the formation of a copper(II) tetrammonium complex. After washing with ammonia the solution needs to be washed with water until pH 7 is reached.

Py-1,2,3-triazole-adamantyl (1). A solution of 2-ethynylpyridine (196 μL, 1.94 mmol) and 1-azidoadamantane (344 mg, 1.94 mmol) in distilled dry tetrahydrofuran (THF) was purged with nitrogen. CuBr (55.6 mg, 0.38 mmol) and PMDTA (*N*,*N*,*'*,*N'*,*N*-pentamethyl diethylenetriamine) (81 μL, 0.38 mmol) in distilled dry THF were added and the solution was stirred at room temperature (RT) for 48 h. Ammonia solution (32%) was added and the solution was stirred for 1 h. Then the solution was extracted between water and diethyl ether. The combined organic phases were washed with brine, dried over MgSO₄ and filtered through silica. The solvent was removed to yield an off-white solid (506 mg, 93%). ¹ H NMR (300 MHz, CDCl₃, δ): 8.49 (ddd, *J* = 4.9, 1.7, 0.9, 1H), 8.16 (s, 1H), 8.12 (dt, *J* = 8.0, 1.0, 1H), 7.69 (td, *J* = 7.8, 1.8, 1H), 7.20–7.06 (m, 1H), 2.21 (s, 10H), 1.70 (d, *J* = 12.7, 7H). MS (ESI+, MeOH): m/z 281.1752 ([M + H]⁺), 303.1579 ([M + Na]⁺).



Py-1,2,3-triazole-benzyl (2). To a solution of 2-ethynylpyridine (1.18 mL, 11.68 mmol) and benzyl azide (1.55 g, 11.64 mmol) in 100 mL MeCN an aqueous solution of CuSO₄ (517 mg, 2.07 mmol) and sodium ascorbate (2.77 g, 13.98 mmol) was added. The last two reagents were dissolved in a minimum volume of water. A bright orange solid formed and the mixture heated up. After addition of 15 mL of MeCN the solid dissolved over 5 h and was left to stir at RT overnight. All solvents were removed under reduced pressure, the orange solid was suspended in ethyl acetate and sonicated. The suspension was filtered and the solvent was removed under reduced pressure to yield an off-white solid. (1.51g, 54%). ¹H NMR (300 MHz, acetone, δ): 8.55 (ddd, *J* = 4.8, 1.7, 0.9, 1H), 8.43 (s, 1H), 8.10 (dt, *J* = 7.9, 1.0, 1H), 7.85 (td, *J* = 7.7, 1.8, 1H), 7.48–7.32 (m, 5H), 7.28 (ddd, *J* = 7.5, 4.8, 1.2, 1H), 2.81 (s, 2H).

Py-1,2,3-triazole-phenyl (3). Aniline (1.02 g, 11.0 mmol) was dissolved in 30 mL of dried and freshly distilled MeCN in a 100 mL round-bottomed flask under N₂ flow and cooled to 0 °C in an ice bath. Tert-butyronitrite (1.74 g, 17 mmol) was added, followed by TMSN₃ (1.31 g, 11.0 mmol). The resulting solution was stirred at RT until thin-layer chromatography (TLC) measurements showed no presence of aniline anymore. 2-Ethynylpyridine (1.13 g, 11.0 mmol) was dissolved in the same round-bottomed flask for a one-pot reaction. CuSO₄·H₂O (206 mg, 0.8 mmol) and sodium ascorbate (660 mg, 3.3 mmol) were added to the solution and the resulting mixture was stirred at RT overnight. The solvent was evaporated under reduced pressure and the product was diluted with dichloromethane, to be extracted three times with 35% ammonia solution. The organic phases were dried over MgSO4, the solvent was evaporated under reduced pressure and the product purified by chromatography on silica gel and dichloromethane/methanol (99:1) as eluent to achieve **7** (1.20 g, 49%). 1 H NMR (300 MHz, $CDCl_3$, δ): 8.69 (s, 1H), 8.60 (dq, J = 6, 1H), 8.29 (dt, J = 9, 1H), 7.82 (m, 3H), 7.56-7.32 (m, 5H). MS (ESI+, MeOH, m/z): calcd. 222.25; found 223.09 [M+H]⁺, 245.08 [M + Na]⁺.

4-Azido-biphenyl. 4-Bromo-biphenyl (1.4 g, 6.01 mmol) and sodium azide (773 mg, 11.9 mmol) in 100 mL ethanol/water 3:1 were degassed by bubbling of nitrogen for 5 min. Copper(I) iodide (228 mg, 1.2 mmol), sodium ascorbate (59 mg, 0.3 mmol), and *N*,*N*'-dimethyl ethylenediamine (0.2 mL, 1.9 mmol) were added and nitrogen was bubbled for another 3 min. The reaction mixture was refluxed for 6 h and the reaction was monitored via TLC. After the reaction was finished a white precipitate was filtered off, washed with water and dried under vacuum. (920 mg, 78%). ¹H NMR (300 MHz, CDCl₃, δ): 2.37 (dd, *J* = 10.6, 4.1, 4H), 2.23 (t, *J* = 7.4, 2H), 2.13 (t, *J* = 7.3, 1H), 1.89 (d, *J* = 8.6, 2H).

Py-1,2,3-triazole-biphenyl (4). 4-Azido-biphenyl (720 mg, 3.4 mmol), 2ethynylpyridine (380 mg, 3.7 mmol), and tetrakis (acetonitrile) copper (1) hexafluorophosphate (273 mg, 0.7 mmol) in dichloromethane/methanol 4:1 were stirred at RT for 14 h. The product started precipitating after 1.5 h, was filtered off, washed with water, and dried under vacuum to yield a lightyellow solid (500 mg, 50%). ¹H NMR (300 MHz, CDCl₃, δ): 8.49 (ddd, J = 4.9, 1.7, 0.9, 1H), 8.16 (s, 1H), 8.12 (dt, J = 8.0, 1.0, 1H), 7.69 (td, J = 7.8, 1.8, 1H), 7.20–7.06 (m, 1H), 2.21 (s, 10H), 1.70 (d, J = 12.7, 7H). General Procedure for the Preparation of Iridium(III) Complexes with

Chloride Counterions: The dimer $(F_2ppy)_2 lr(\mu-Cl)_2 lr(F_2ppy)_2$ and the according 1,2,3-triazole were stirred in dichloromethane/ethanol 5:1 overnight. The starting materials were solubilized within 45 min. The solvents were removed under reduced pressure. The resulting yellow solids were dissolved in acetonitrile and filtered through celite. The solvent was removed under reduced pressure and the solid was recrystallized from ethanol three times and dried under vacuum.

General Procedure for Ion Exchange on the Iridium(III) Complexes: The chloride counterion was exchanged to the desired tetrafluoroborate **a** or hexafluorophosphate **b** by stirring the compound in a dichloromethane/ methanol mixture (10:1) with sodium tetrafluorborate or ammonium hexafluorophosphate, respectively. The according complex with chloride counterion was dissolved in an excess of dichloromethane. Another solution of 15 equivalents of either ammonium hexafluorophosphate or sodium tetrafluorborate in methanol was added and the resulting turbid mixture was stirred for 18 h at RT. After the removal of the solvents the crude reaction mixture was suspended in water and sonicated for 5 min. The precipitate was filtered off and washed with water excessively in order



to remove the excess of the sodium or ammonium salts, respectively. After drying, the compounds were recrystallized from ethanol four times and dried under vacuum afterwards.

(F₂ppy)₂ Ir Py-1,2,3-triaz-adamantyl PF₆ (5b). ¹H NMR (300 MHz, CD₂Cl₂, δ): 8.78 (s, 1H), 8.31 (d, J = 7.9, 3H), 8.08 (td, J = 7.8, 1.6, 1H), 7.84 (dt, J = 7.6, 5.6, 3H), 7.52 (ddd, J = 17.1, 5.8, 0.8, 2H), 7.36 (ddd, J = 7.6, 5.5, 1.3, 1H), 7.06 (dddd, J = 18.1, 7.3, 5.9, 1.4, 2H), 6.57 (dddd, J = 18.0, 12.5, 9.2, 2.3, 2H), 5.74 (ddd, J = 10.6, 8.6, 2.4, 2H), 2.25 (s, 3H), 2.20 (d, J = 2.7, 6H), 1.85–1.71 (m, 7H). ¹⁹F NMR (282 MHz, CD₂Cl₂, δ): -71.32 (s, 3H), -73.83 (s, 3H), -106.64 (dt, J = 10.8, 9.0, 1H), -107.76–107.96 (m, 1H), -108.94–109.14 (m, 1H), -110.15 (dd, J = 17.9, 7.5, 1H). Mass L1-53-01 MS (ESI + , MeOH, m/z): [M]⁺ 853.2224. Anal. calcd. for C₃₉H₃₂F₁₀IrN₆P: C 46.94, H 3.23, N 8.42; found: C 46.26, H 3.27, N 8.01.

 $\begin{array}{l} (F_2ppy)_2 \mbox{ Ir Py-1,2,3-triaz-benzyl BF}_4 \mbox{ (fa}_2)^{-1} \mbox{ H} NMR \mbox{ (300 MHz, CD}_2Cl_2, \\ \delta): 9.04 \mbox{ (s, 1H), 8.38-8.25 \mbox{ (m, 3H), 8.06 \mbox{ (tt, } J = 7.9, 3.8, 1H), 7.90-7.76 \mbox{ (m, 3H), 7.68-7.59 \mbox{ (m, 1H), 7.51-7.43 \mbox{ (m, 1H), 7.42-7.29 \mbox{ (m, 6H), 7.04 \mbox{ (ddd, } J = 17.0, 7.3, 5.9, 1.4, 2H), 6.58 \mbox{ (dddd, } J = 14.8, 12.5, 9.2, 2.4, 2H), \\ 5.77 \mbox{ (ddd, } J = 14.6, 8.5, 2.3, 2H), 5.70-5.55 \mbox{ (m, 2H), 1.64 \mbox{ (s, 2H)}.}^{19} \mbox{ F} NMR \mbox{ (282 MHz, CD}_2Cl_2, \mbox{ (b)}: -106.65 \mbox{ (dt, } J = 10.8, 9.0, 1H), -107.48 \mbox{ (dt, } J = 10.4, 9.0, 1H), -108.90-109.14 \mbox{ (m, 1H), -109.71-109.94 \mbox{ (m, 1H)}, -151.35-151.49 \mbox{ (m, 3H)}. MS \mbox{ (ESI +, MeOH, m/z): } [M]^+ \mbox{ 809.1587. HRMS \mbox{ [M]}^+ \mbox{ calcd for } C_{36}H_{24}BF_8IrN_6: C \mbox{ 48.28, H 2.70, N 9.38; found: C \mbox{ 47.90, H 2.74, N 9.31.} \end{array}$

 $\begin{array}{l} (F_2ppy)_2 \mbox{ Ir Py-1,2,3-triaz-benzyl PF}_6 \mbox{ (6b). }^{1}\mbox{ H NMR } (300\mbox{ MHz, CD}_2Cl_2, \\ \delta): 8.63 \mbox{ (s, 1H), 8.31 } (d, {\it J}=7.0, 2H), 8.14 \mbox{ (d, {\it J}=7.5, 1H), 8.05 } (td, {\it J}=7.8, \\ 1.6, 1H), 7.84 \mbox{ (t, {\it J}=6.8, 3H), 7.63 } (d, {\it J}=5.0, 1H), 7.46 \mbox{ (d, {\it J}=5.0, 1H), } \\ 7.43-7.28 \mbox{ (m, 6H), 7.13-6.97 } (m, 2H), 6.67-6.51 \mbox{ (m, 2H), 5.81-5.71 } (m, \\ 2H), 5.61 \mbox{ (s, 2H), 1.19 } (t, {\it J}=7.0, 2H). \mbox{ }^{19}\mbox{ F NMR } (282\mbox{ MHz, CD}_2Cl_2, \delta): \\ -71.39 \mbox{ (s, 3H), -73.90 } (s, 3H), -106.59 \mbox{ (dt, {\it J}=10.9, 9.0, 1H), -107.28-107.47 } (m, 1H), -108.95 \mbox{ (t, {\it J}=11.7, 1H), -109.77 } \mbox{ (t, {\it J}=11.5, 1H). MS } \\ (ESI +, MeOH, m/z): \mbox{ [M]}^+ \mbox{ 809.1642. Anal. calcd. for $C_{36}H_{24}F_{10}IrN_6P: C 45.33, H 2.54, N 8.81; found: \\ C 45.29, H 2.51, N 8.71. \end{array}$

(F₂ppy)₂ Ir Py-1,2,3-triaz-phenyl PF₆ (7b). ¹H NMR (300 MHz, CDCl₃, δ): 9.77 (s, 1H), 8.75 (d, J = 9, 1H), 8.25 (d, J = 9, 2H), 8.07 (td, J = 9, 3, 1H), 7.84–7.66 (m, 6H), 7.47 (m, 4H), 7.30 (t, J = 6; 1H), 7.08–6.98 (m, 2H), 6.56–6.43 (m, 2H), 5.65 (td, J = 9, 1.5, 2H). MS (ESI+, MeOH, m/z): [M]⁺ calcd. 795.95; found: 795.15. Anal. calcd. for C₃₅H₂₂F₁₀IrN₆P: C 44.73, H 2.36, N 8.94; found: C 40.26, H 2.57, N 8.27.

(F₂ppy)₂ Ir Py-1,2,3-triaz-biphenyl BF₄ (8a). ¹H NMR (300 MHz, CD₂Cl₂, δ): 9.65 (s, 1H), 8.67 (d, J = 7.8, 1H), 8.34 (d, J = 9.2, 2H), 8.15 (t, J = 7.9, 1H), 7.97 (d, J = 8.8, 2H), 7.92–7.77 (m, 6H), 7.64 (d, J = 6.9, 2H), 7.55 (d, J = 5.0, 1H), 7.44 (dt, J = 22.2, 7.0, 4H), 7.15–7.02 (m, 2H), 6.62 (ddd, J = 24.5, 12.1, 6.9, 2H), 5.84–5.74 (m, 2H), 5.33 (s, 3H). ¹⁹F NMR (282 MHz, CD₂Cl₂, δ): –106.34–106.74 (m, 1H), –107.37–107.71 (m, 1H), –108.96 (t, J = 11.7, 1H), –109.84 (t, J = 11.5, 1H), –151.10 (dd, J = 2.3, 1.1, 4H). MS (ESI +, MeOH, m/z): [M]⁺ 871.1777. HRMS calcd. [M]⁺ 871.1781; found 871.1777. Crystals were grown from CH₂Cl₂. Anal. calcd. for C4₁H₂₆BF₈IrN₆ + CH₂Cl₂: C 48.38, H 2.71, N 8.06; found: C 48.25, H 2.78, N 7.95.

(F₂ppy)₂ Ir Py-1,2,3-triaz-biphenyl PF₆ (8b). ¹H NMR (300 MHz, CD₂Cl₂, δ): 9.28 (s, 1H), 8.45 (d, J = 7.9, 1H), 8.33 (dd, J = 8.4, 1.0, 2H), 8.13 (td, J = 7.8, 1.6, 1H), 7.97–7.72 (m, 8H), 7.67–7.59 (m, 2H), 7.55 (dd, J = 5.9,



1818



0.9, 1H), 7.51–7.33 (m, 4H), 7.09 (dddd, J = 15.9, 7.4, 5.9, 1.3, 2H), 6.69– 6.49 (m, 2H), 5.83–5.74 (m, 2H), 5.32–5.29 (m, 1H). ¹⁹F NMR (282 MHz, CD₂Cl₂, δ): –71.04 (s, 3H), –73.56 (s, 3H), –106.48 (dt, J = 10.8, 8.9, 1H), –107.38–107.59 (m, 1H), –108.81–109.02 (m, 1H), –109.71–109.91 (m, 1H). MS (ESI+, MeOH, m/z): [M]⁺ 871.1757. Anal. calcd. for C₄₁H₂₆F₁₀IrN₆P + CH₂Cl₂: 45.83, H 2.56, N 7.63; found: C 46.30, H 2.86, N 7.68.

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- J. K. Lee, D. S. Yoo, E. S. Handy, M. F. Rubner, *Appl. Phys. Lett.* 1996, 69, 1686.
- [2] J. D. Slinker, J. A. DeFranco, M. J. Jaquith, W. R. Silveira, Y.-W. Zhong, J. M. Moran-Mirabal, H. G. Craighead, H. D. Abruna, J. A. Marohn, G. G. Malliaras, *Nat. Mater.* **2007**, *6*, 894.
- [3] Q. Pei, G. Yu, C. Zhang, Y. Yang, A. J. Heeger, Science 1995, 269, 1086.
- [4] J. C. de Mello, N. Tessler, S. C. Graham, X. Li, A. B. Holmes, R. H. Friend, Synth. Met. 1997, 85, 1277.
- [5] J. C. de Mello, N. Tessler, S. C. Graham, R. H. Friend, Phys. Rev. B 1998, 57, 12951.
- [6] C. H. Lyons, E. D. Abbas, J. K. Lee, M. F. Rubner, J. Am. Chem. Soc. 1998, 120, 12100.
- [7] S. Welter, K. Brunner, J. W. Hofstraat, L. De Cola, Nature 2003, 421, 54.
- [8] D. Di Censo, S. Fantacci, F. De Angelis, C. Klein, N. Evans, K. Kalyanasundaram, H. J. Bolink, M. Gratzel, M. K. Nazeeruddin, *Inorg. Chem.* 2008, 47, 980.
- [9] C. Rothe, C.-J. Chiang, V. Jankus, K. Abdullah, X. Zeng, R. Jitchati, A. S. Batsanov, M. R. Bryce, A. P. Monkman, *Adv. Funct. Mater.* 2009, 19, 2038.
- [10] L. He, L. Duan, J. Qiao, R. Wang, P. Wei, L. Wang, Y. Qiu, Adv. Funct. Mater. 2008, 18, 2123.
- [11] X. Zeng, M. Tavasli, Igor F. Perepichka, Andrei S. Batsanov, Martin R. Bryce, C.-J. Chiang, C. Rothe, Andrew P. Monkman, *Chem. -Eur. J.* 2008, 14, 933.
- [12] H.-C. Su, H.-F. Chen, C.-C. Wu, K.-T. Wong, Chem.-Asian J. 2008, 3, 1922.
- [13] H.-C. Su, H.-F. Chen, F.-C. Fang, C.-C. Liu, C.-C. Wu, K.-T. Wong, Y.-H. Liu, S.-M. Peng, J. Am. Chem. Soc. 2008, 130, 3413.
- [14] S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, R. D. Costa, E. Orti, D. Repetto, H. J. Bolink, *J. Am. Chem. Soc.* **2008**, *130*, 14944.
- [15] V. Marin, E. Holder, R. Hoogenboom, U. S. Schubert, Chem. Soc. Rev. 2007, 36, 618.
- [16] H.-C. Su, C.-C. Wu, F.-C. Fang, K.-T. Wong, Appl. Phys. Lett. 2006, 89, 261118.
- [17] T. Sajoto, P. I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M. E. Thompson, R. J. Holmes, S. R. Forrest, *Inorg. Chem.* 2005, 44, 7992.
- [18] F. Neve, M. La Deda, A. Crispini, A. Bellusci, F. Puntoriero, S. Campagna, Organometallics 2004, 23, 5856.
- [19] J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, G. G. Malliaras, J. Am. Chem. Soc. 2004, 126, 2763.
- [20] L. Wang, B. Du, Y. Cao, J. Wang, Proc. SPIE 2007, 6828, 6828OI.
- [21] J. D. Slinker, C. Y. Koh, G. G. Malliaras, M. S. Lowry, S. Bernhard, Appl. Phys. Lett. 2005, 86, 173506.
- [22] M. Buda, G. Kalyuzhny, A. J. Bard, J. Am. Chem. Soc. 2002, 124, 6090.



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- [23] G. Kalyuzhny, M. Buda, J. McNeill, P. Barbara, A. J. Bard, J. Am. Chem. Soc. 2003, 125, 6272.
- [24] L. J. Soltzberg, J. D. Slinker, S. Flores-Torres, D. A. Bernards, G. G. Malliaras, H. D. Abruna, J.-S. Kim, R. H. Friend, M. D. Kaplan, V. Goldberg, J. Am. Chem. Soc. 2006, 128, 7761.
- [25] G. Santos, F. Fonseca, A. M. Andrade, A. O. T. Patrocínio, S. K. Mizoguchi, N. Y. M. Iha, M. Peres, T. Monteiro, L. Pereira, *Phys. Status Solidi A* 2008, 205, 2057.
- [26] F. Z. Wang, J. F. Fan, X. N. Dang, X. Fan, P. Wang, X. H. Wan, D. C. Zou, S. H. Kim, D. N. Lee, B. H. Kim, J. Appl. Phys. 2008, 103, 104509.
- [27] S. Bernhard, X. Gao, G. G. Malliaras, H. D. Abruña, Adv. Mater. 2002, 14, 433.
- [28] W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li, Z. Hui, J. Am. Chem. Soc. 2004, 126, 7639.
- [29] T. Li, Y. Du, E. Wang, Chem.-Asian J. 2008, 3, 1942.
- [30] Y.-M. Wang, F. Teng, Y.-B. Hou, Z. Xu, Y.-S. Wang, W.-F. Fu, Appl. Phys. Lett. 2005, 87, 233512.
- [31] Q. Zhang, Q. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, Adv. Funct. Mater. 2006, 16, 1203.
- [32] S. C. Yu, C. C. Kwok, W. K. Chan, C. M. Che, Adv. Mater. 2003, 15, 1643.
- [33] H. J. Bolink, E. Coronado, R. D. Costa, N. Lardies, E. Orti, *Inorg. Chem.* 2008, 47, 9149.
- [34] H. Z. Xie, M. W. Liu, O. Y. Wang, X. H. Zhang, C. S. Lee, L. S. Hung, S. T. Lee, P. F. Teng, H. L. Kwong, H. Zheng, C. M. Che, *Adv. Mater.* 2001, *13*, 1245.
- [35] E. Orselli, G. S. Kottas, A. E. Konradsson, P. Coppo, R. Foehlich, L. De Cola, A. van Dijken, M. Buchel, H. Borner, *Inorg. Chem.* 2007, 46, 11082.
- [36] C. Dragonetti, S. Righetto, D. Roberto, R. Ugo, A. Valore, S. Fantacci, A. Sgamellotti, F. D. Angelis, *Chem. Commun.* 2007, 4116.
- [37] M. S. Lowry, S. Bernhard, Chem. -Eur. J. 2006, 12, 7970.
- [38] K. R. Lee, M.-S. Eum, C. S. Chin, S. C. Lee, I. J. Kim, Y. S. Kim, Y. Kim, S.-J. Kim, N. H. Hur, *Dalton Trans.* 2009, 3650.
- [39] L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, Top. Curr. Chem. 2007, 281, 143.
- [40] H. J. Bolink, L. Cappelli, E. Coronado, M. Gratzel, E. Orti, R. D. Costa, P. M. Viruela, M. K. Nazeeruddin, J. Am. Chem. Soc. 2006, 128, 14786.
- [41] H. J. Bolink, L. Cappelli, S. Cheylan, E. Coronado, R. D. Costa, N. Lardies, M. K. Nazeeruddin, E. Orti, J. Mater. Chem. 2007, 17, 5032.
- [42] H. J. Bolink, Mater. Res. Soc. Symp. Proc. 2007, 965.
- [43] H. J. Bolink, E. Coronado, R. D. Costa, E. Ortí, M. Sessolo, S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, *Adv. Mater.* 2008, 20, 3910.
- [44] F. De Angelis, S. Fantacci, N. Evans, C. Klein, S. M. Zakeeruddin, J.-E. Moser, K. Kalyanasundaram, H. J. Bolink, M. Gratzel, M. K. Nazeeruddin, *Inorg. Chem.* 2007, 46, 5989.
- [45] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, Angew. Chem. Int. Ed. 2002, 41, 2596.
- [46] B. Beyer, C. Ulbricht, D. Escudero, C. Friebe, A. Winter, L. Gonzalez, U. S. Schubert, Organometallics 2009, 28, 5478.
- [47] B. H. Lipshutz, D. M. Nihan, E. Vinogradova, B. R. Taft, Z. V. Bošković, Org. Lett. 2008, 10, 4279.
- [48] M. Felici, P. Contreras-Carballada, Y. Vida, J. M. M. Smits, R. J. M. Nolte, L. D. Cola, R. M. Williams, M. C. Feiters, *Chem. -Eur. J.* **2009**, *15*, 13124.
- [49] Y. You, S. Y. Park, J. Am. Chem. Soc. 2005, 127, 12438.
- [50] P.-T. Chou, Y. Chi, Eur. J. Inorg. Chem. 2006, 3319.
- [51] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* 2001, 40, 1704.
- [52] M. Polson, S. Fracasso, V. Bertolasi, M. Ravaglia, F. Scandola, Inorg. Chem. 2004, 43, 1950.
- [53] I. Avilov, P. Minoofar, J. Cornil, L. De Cola, J. Am. Chem. Soc. 2007, 129, 8247.
- [54] L. He, J. Qiao, L. Duan, G. Dong, D. Zhang, L. Wang, Y. Qiu, Adv. Funct. Mater. 2009, 19, 2950.
- [55] S. T. Parker, J. D. Slinker, M. S. Lowry, M. P. Cox, S. Bernhard, G. G. Malliaras, *Chem. Mater.* 2005, *17*, 3187.







- [56] Tetrabutyl ammonium hexafluorophosphate, was dried at 130 $^{\circ}\mathrm{C}$ and stored in a closed vial in a dessicator between experiments.
- [57] Acetonitrile was freshly distilled from $\mathsf{P}_2\mathsf{O}_5.$
- [58] B. V. Nonius, data collection **1998**.
- [59] Z. Otwinowski, W. Minor, in Macromolecular Crystallography, Part A, Vol. 276, Academic Press Inc, San Diego 1997, 307.
- [60] R. H. Blessing, Acta Crystalogr, Sect. A 1995, 51, 33.
- [61] R. H. Blessing, J. Appl. Crystallogr. 1997, 30, 421.
- [62] Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Crystallogr, Sect. A 2003, 59, 228.
- [63] G. M. Sheldrick, Acta Crystallogr, Sect. A 1990, 46, 467.
- [64] G. M. Sheldrick, program SHELXL-97, Universität Göttingen, Göttingen, Germany 1997.

- [65] E. Keller, program SCHAKAL, Universität Freiburg 1997.
- [66] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, New York 1980.
- [67] W. C. Still, M. Kahn, A. Mitra, J. Org. Chem. 2002, 43, 2923.
- [68] M. Obata, A. Kitamura, A. Mori, C. Kameyama, J. A. Czaplewska, R. Tanaka, I. Kinoshita, T. Kusumoto, H. Hashimoto, M. Harada, Y. Mikata, T. Funabiki, S. Yano, *Dalton Trans.* **2008**, 3292.
- [69] C. Richardson, C. M. Fitchett, F. R. Keene, P. J. Steel, Dalton Trans. 2008, 2534.
- [70] S. Diez-Gonzalez, E. D. Stevens, S. P. Nolan, Chem. Commun. 2008, 4747.
- [71] I. S. Park, M. S. Kwon, Y. Kim, J. S. Lee, J. Park, Org. Lett. 2008, 10, 497.
- [72] T. R. Chan, V. V. Fokin, QSAR Comb. Sci. 2007, 26, 1274.
- [73] K. Barral, A. D. Moorhouse, J. E. Moses, Org. Lett. 2007, 9, 1809.

1820