

DOI: 10.1002/ejic.201200061

Postfunctionalization of Luminescent Bipyridine Pt^{II} Bisacetylides by Click Chemistry

Ilona Stengel,^[a,b] Cristian A. Strassert,^[b,c] Edward A. Plummer,^[b,c] Chen-Han Chien,^[c] Luisa De Cola,^{*[b,c]} and Peter Bäuerle^{*[a,b]}

Keywords: Platinum / Click chemistry / Luminescence

The synthesis of a family of differently substituted 5- and 4,4'-ethynyl-bpy Pt^{II} bisacetylide complexes (bpy = 2,2'-bipyridine) and their postfunctionalization using click chemistry is described. Cu^I-catalyzed azide–alkyne [3+2] cycloaddition was an efficient method to decorate the Pt^{II} complexes with a manifold of moieties in high yields. The absorption and emission properties and the electrochemical behaviour of all of the complexes have been investigated. The studied compounds emit at room temperature between 598 and 660 nm, reaching photoluminescence quantum yields of 0.33 in solution. The bright luminescent properties of the unsub-

Introduction

Luminescent square-planar PtII complexes have attracted great attention in different research fields over the past 10-20 years. Different series of compounds with aromatic ligands have been synthesized and show strong emission from intraligand (IL) or metal-to-ligand charge transfer (MLCT) excited states, which makes them potential candidates for electroluminescent devices.^[1] Substitution of the coordinated ligands with suitable donor or acceptor groups allows the nature of the excited states to be tuned, thus, enabling the synthesis of complexes with a pronounced MLCT character, which can find application as materials for sensors^[2] or nonlinear optics.^[3] In contrast to octahedral Ir^{III} complexes, which have been successfully applied and commercialized as luminescent materials in organic light-emitting diodes (OLEDs), square-planar Pt^{II} complexes have not yet reached the required performance mainly due to their tendency to aggregate and lower stability. On the other hand, Pt–Pt and π - π stacking interac-

- [a] Institute of Organic Chemistry II and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany
- E-mail: peter.baeuerle@uni-ulm.de
- [b] Dutch Polymer Institute (DPI),
- P.O. Box 902, 5600 AX Eindhöven, The Netherlands
 [c] Center for Nanotechnology, University of Münster, Heisenbergstrasse 11, 48149 Münster, Germany
- E-mail: decola@uni-muenster.de
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201200061.

stituted bpy Pt^{II} bisacetylide complex remained unaffected upon click-functionalization as the resulting triazole substituent has no significant influence on the nonradiative decay rate constant. This route opens new possibilities for to control the bulk of the complexes, their solubility, and their further extension or immobilization on macromolecules, polymers and surfaces without affecting their intrinsic properties. Two derivatives were selected as triplet emitter molecules in solution-processed polymer-based organic light-emitting devices.

tions in these compounds can be used as a tool in supramolecular chemistry, self-assembled materials and vapoluminescent sensors.^[4,5]

Organometallic synthesis has provided a huge variety of differently substituted PtII complexes, such as cyclometallated compounds,^[6] derivatives with chelating ligands such as terpyridine,^[7] bipyridine (bpy)^[8,9] and their analogous Nchelates.^[10] The most brightly luminescent Pt^{II} complexes are those with strong donor ligands on one side and aromatic π -accepting ligands on the other side. Strong donors such as acetylides push the unoccupied $d_{x^2-y^2}$ orbital up in energy and inhibit the population of d-d excited states, which would otherwise facilitate nonradiative decay.^[11] Aromatic ligands provide lowest unoccupied molecular orbitals (LUMOs) for low-energy emissive states, mostly of ligand centred or MLCT nature. Furthermore, the planarity of the complex is an important issue, as a higher rigidity diminishes the tendency for nonradiative decay, thus, enhancing the photoluminescence quantum vield (PLQY).^[9c-9d,12]

Bpy Pt^{II} bisacetylides and their photophysical properties have been previously investigated by several groups. The first derivatives of this kind were 1,10-phenanthroline Pt^{II} bis(phenylacetylide), synthesized and characterized in 1994 by Che and coworkers,^[8f] followed by (4,4'-dimethyl-bpy) Pt^{II} bis(phenylacetylide) in 1997.^[8g] In general, the complexes showed characteristic MLCT absorption and unstructured emission bands in solution at room temperature, which reached PLQYs of up to 0.75.^[9d] Furthermore, the emission colour is tunable over a wide range depending on the electron-donating or -withdrawing character of the substituents attached to the coordinated ligands. Two interesting series of compounds have been synthesized by the groups of Eisenberg,^[8h] who varied the substituents at the phenylacetylide, and Schanze,[8j] who introduced different functionalities at the bpy ligand in order to understand their effect on the photophysical properties. It was observed that the absorption and the emission were redshifted as the electron-donating character of the substituents at the phenylacetylide increased, but the effect is much more pronounced on the emission than on the absorption. Likewise, a redshift was observed if the electron-donating ability of the substituents at the bpy decreased. Significant work regarding the nature of the lowest energy excited state of these compounds has been carried out by Castellano and coworkers.^[9] By comparing phenyl-, tert-butyl- and trimethylsilylacetylide ligands and their influence on the photophysics of bpy Pt^{II} complexes, they systematically investigated their molecular orbital landscape.^[9a-9b] All of their observations are consistent with a metal- and partly acetylide-localized highest occupied molecular orbital (HOMO), which increased in energy with increased electron density, and with a bpy-centred LUMO, which decreased in energy with decreased electron density.

A disadvantage of the high rigidity of such compounds is their poor solubility in organic solvents. However, high solubilities are required for solution processing, e.g. inkjet printing or spin coating of phosphorescent materials. In this respect, Pt^{II} complexes have been covalently bound to soluble polymers, either in the backbone or as pendant groups.^[13]

In this work, we discuss click chemistry as a method to postfunctionalize Pt^{II} complexes, e.g. with solubilizing groups. The term click chemistry was coined in 2001 by Sharpless et al.,^[14] and Cu^I-catalyzed azide–alkyne [3+2] cycloaddition (CuAAC) has become a versatile method to link azides to ethynyl-substituted precursors since then.^[15] We intended to find out if (a) the method is adaptable to Pt^{II} coordination compounds, even in the presence of coordinated acetylide units, and (b) how the resulting triazolyl subsitutents influence the photophysical properties. Therefore, we synthesized a series of different ethynyl- and triazolyl-substituted bpy PtII bisacetylides and investigated their absorption, emission and electrochemical properties. Furthermore, we successfully used two representative derivatives as dopants in solution-processed polymer-based light-emitting devices (PLEDs). The performance of the simple devices, using polyvinylcarbzole (PVK) as a host matrix and the Pt^{II} complexes as dopants, proved that the compounds are also suitable for electroluminescence.

Results and Discussion

Synthesis

The complexes can be categorized into two series, namely, 5-substituted and 4,4'-disubstituted bpy Pt^{II} bisace-tylides. The bpy ligands, 5-(trimethylsilylethynyl)-2,2'-bi-

pyridine^[16] and 4,4'-bis(trimethylsilylethynyl)-2,2'-bipyridine.^[17] were introduced in a ligand exchange reaction with $cis-(DMSO)_2Pt^{II}Cl_2^{[18]}$ (DMSO = dimethyl sulfoxide) in acetonitrile at room temperature. The corresponding bpy Pt^{II} dichlorides 1^[19] and 5 were obtained in high yield. The acetylide ligands were attached using a method initially described by Sonogashira,^[20] which has been previously applied for similar derivatives.^[8g,8k-81] During our synthetic work, we noticed that the final click products showed lower solubility in organic solvents than their precursors. Hence, we introduced not only phenyl acetylides, but also 4-hexylphenyl acetylides with solubilizing alkyl chains. In this respect, trimethylsilyl (TMS)-protected compounds 2 and 6 were obtained under mild reaction conditions in good yields from 73–97% (Scheme 1). The corresponding deprotected ethynyl-functionalized complexes 3 and 7 were isolated by stirring 2 and 6 with potassium fluoride in dichloromethane and methanol at room temperature for several hours. The formation of bimetallic PtIICuI complexes was observed by mass spectrometry of the crude products and has been described in the literature before.^[21] The Cu^I cations are able to be coordinated by the two triple bonds in the PtII bisacetylide complexes and can be removed by aqueous workup with ammonia by oxidizing the Cu^I species and by column chromatography.

The click reaction with phenyl^[22] or benzyl^[23] azides was either performed using the deprotected ethynyl complexes 3 and 7, or directly after the in situ deprotection of TMSprotected 2 and 6 with potassium fluoride. The more convenient in situ deprotection was therefore chosen as a standard protocol, although both methods proceeded in high yields. Cu(CH₃CN)₄PF₆ was used as the catalyst, and elemental copper was added to reduce any oxidized Cu^{II}. The addition of ethyldiisopropylamine (DIPEA) as a base resulted in faster reactions because it supports the deprotonation of the Cu^I-complexed acetylene.^[15c] The reaction progress was monitored by TLC. Typically, reaction times ranged from 24 h to three days. The clicked Pt^{II} complexes 4 and 8 were obtained in 73–97% yield. Complex 8e, which bears *n*-hexyl chains at the phenyl triazole unit was synthesized by using 4-hexylphenyl azide^[24] in the click reaction. It can be directly compared to 8d, which is an isomer that bears the hexyl chains at the phenyl acetylide units, and to 8c, a closely related derivative without alkyl chains. In general, the 5-substituted bpy compounds were slightly more soluble than their 4,4'-disubstituted analogues.

All complexes were fully characterized by ¹H and, if the solubility was sufficient, ¹³C NMR spectroscopy as well as MALDI-TOF MS, FTIR spectroscopy and elemental analysis. The compounds do not show defined melting points, but decomposed above 150 °C. Doublets at around 9.7 ppm (³J = 6 Hz) are characteristic ¹H NMR signals for 6-H of the bpy ligand in 4,4'-substituted bpy Pt^{II} complexes. For the 5-substituted derivatives, two doublets were observed at around 9.6 (³J = 6 Hz) and 10.0 (⁴J = 2 Hz) ppm for the protons in the 6'- and 6-positions, respectively. Singlets were observed for the triazole protons at 7.9–8.4 ppm for the 5-substituted derivatives in CD₂Cl₂ at

TMS

TMS

TMS

1

h

 R^1

C.

5



Scheme 1. Synthesis of (a) 2 and 6: CuI, iPr₂NH, CH₂Cl₂, phenylacetylide/4-hexylphenylacetylide, room temp., 12 h, (b) 3 and 7: KF, MeOH, DCM, room temp., 12 h, (c) 4 and 8: KF, phenyl-/benzyl-/4-hexylphenyl azide, Cu(CH₃CN)₄PF₆, Cu⁰, DIPEA, CH₂Cl₂/methanol (4:1), room temp., 3 d.

 $7a R^1 = H R^2 = H (65\%)$

7b $R^1 = H$, $R^2 = nHex$ (95%)

25 °C, which shifted to 8.7-9.2 ppm in [D₆]DMSO at 100 °C. For the 4,4'-substituted derivatives, the singlets due to the triazole protons typically appeared downfield-shifted at 8.4–9.0 ppm in CD₂Cl₂ at 25 °C and 9.0–9.7 ppm in [D₆]-DMSO at 100 °C. MALDI-TOF MS were recorded using dithranol as the matrix. The molecular mass peak was obtained for all compounds, as well as peaks from the fragmentation products, mostly corresponding to the loss of one or two phenylacetylides. In most cases, a peak corresponding to the dimer was also observed.

Photophysical Characterization

The photophysical data of the compounds is summarized in Table 1. Absorption spectra were recorded in dicholoromethane (DCM) at room temperature and display characteristic IL π - π * transitions between 250 and 350 nm from the coordinated bipyridine, as well as MLCT bands spanning from 350 to 550 nm. The molar extinction coefficients of the MLCT absorption maxima range from 5900- $6400 \text{ M}^{-1} \text{ cm}^{-1}$ for the 5-substituted derivatives, and from $8500-12700 \text{ M}^{-1} \text{ cm}^{-1}$ for the 4,4'-substituted compounds.

The absorption bands of the complexes appear redshifted and broadened in both the IL and MLCT regions compared with the unsubstituted reference compound 2,2'-bipyridinebis(phenylethynyl)platinum(II) (9).^[21]

8d $R^2 = nHex$, $R^3 = phenyl$ (73%)

8e R^2 = H, R^3 = 4-*n*-hexylphenyl (79%)

Representative absorption spectra are depicted in Figure 1, which show shifts that originate from the different substitution patterns. The introduction of conjugated alkynyl groups at the bipyridine ligand causes a redshift and broadening of the absorption bands, as illustrated by 5-(TMS-ethynyl)bpyPt^{II} (2a) compared with 9 (Figure 1a). The absorption is further redshifted upon introduction of *n*hexyl chains (e.g. 2b), which enhance the electron-donating character of the coordinated phenylacetylides, thus, raising the HOMO. However, the molar extinction coefficient is not affected by the hexyl chains. As expected, no remarkable difference was observed between 5-substituted complexes bearing TMS-protected or unprotected ethynyl groups at the bpy ligand (cf. 2a and 3a). Noticeably, however, a blueshift of the MLCT absorption and an additional broadening of the IL absorption are observed, for instance, by comparison of the 5-ethynyl-bpy Pt^{II} complex 3a and its clicked derivative 4a (Figure 1b). It is known that click

FULL PAPER

Table 1. Photophysical parameters of the investigated complexes.	able 1. Photophysical parameters of the investigated compl	lexes. ^{[a}
------------------------------------------------------------------	------------------------------------------------------------	----------------------

	$ \begin{array}{l} \lambda_{abs} \ [nm]^{[b]} \\ (\varepsilon \ [M^{-1} \ cm^{-1}]) \end{array} $	λ _{em} ^[b] [nm]	λ _{em} 77 K ^[c] [nm]	${\varPhi}^{[{ m b},{ m d}]}$	τ ^[b] [ns]	$k_{ m r} = [10^5 \ { m s}^{-1}]$	$k_{ m nr} \ [10^5 \ m s^{-1}]$	τ 77 K ^[e] [μs]
2a	425 (6300)	610	533	0.09	321	2.8	28	1.5 (27%), 3.8 (73%)
2b	432 (6300)	638	552	0.02	85	2.4	120	2.1 (17%), 3.9 (83%)
3a	424 (6100)	612	539	0.08	251	3.2	37	1.3 (28%), 3.6 (72%)
3b	429 (6200)	645	546	0.03	66	4.5	150	1.7 (17%), 3.9 (83%)
4a	412 (5900)	598	535	0.24	696	3.4	11	1.4 (10%), 4.0 (90%)
4b	418 (6400)	623	543	0.08	222	3.6	41	3.1 (55%), 5.1 (45%)
4c	413 (6000)	605	532	0.19	613	3.1	13	1.6 (7%), 4.2 (93%)
4d	416 (5900)	628	540	0.05	186	2.7	51	2.4 (33%), 4.9 (67%)
6a	430 (11000)	626	536	0.18	483	3.7	17	0.5 (28%), 2.1 (72%)
6b	435 (10800)	653	560	0.05	138	3.6	69	1.4 (29%), 3.6 (71%)
7a	432 (9100)	631	554	0.10	330	3.0	27	0.4 (10%), 3.6 (90%)
7b	435 (8500)	660	581	0.02	90	2.2	110	1.1 (13%), 3.6 (87%)
8a	418 (10800)	603	536	0.33	777	4.2	8.6	3.5 (100%)
8b	422 (10800)	608	531	0.08	273	2.9	34	1.9 (41%), 4.0 (59%)
8c	421 (11200)	619	[528] ^[f] 555	0.18	688	2.6	12	2.6 (38%), 4.8 (62%)
8d	426 (11500)	626	508	0.10	218	4.6	41	2.5 (65%), 8.6 (35%)
8e	420 (12700)	604	556	0.25	709	3.5	11	3.6 (100%)
9	405 (7100)	577	509	0.28	749	3.7	9.6	3.1 (100%)

[a] Φ = Photoluminescence quantum yield, exciting at the MLCT absorption maximum. τ = Emission decay lifetime, monitored at the maximum of the emission spectrum, $\lambda_{Ex} = 431$ nm. Radiative decay rate constant, $k_r = \Phi/\tau$. Nonradiative decay rate constant, $k_{nr} = (1 - \Phi)/\tau$. [b] All measurements were carried out in spectroscopic grade DCM at $c \approx 10^{-5} \text{ mol L}^{-1}$. Measured at room temp. (298 K). [c] Measured at 77 K in DCM glassy matrix. [d] Measured with an integrating sphere. Quantum yields and lifetimes correspond to deaerated solutions. [e] Lifetimes at 77 K in a DCM glassy matrix, monitoring the most energetic emission maximum; relative amplitudes of the components are given in brackets. [f] The maximum of the additional shoulder is given in brackets.

chemistry is not a suitable method for the synthesis of extended π -conjugated systems, and it has been shown that if conjugated building blocks are directly connected through the resulting 1,2,3-triazol-4-yl moiety, the elongated systems hardly display any redshift in the absorption spectra.^[25] Steric effects that induce a twist of the triazole ring and weaken the mesomeric interactions through the nitrogen atoms involved are considered to be responsible for the poorly mediated conjugation. As a result, the triazole substituent constitutes a σ donor rather than a π^* acceptor. Indeed, almost no difference is observed in the absorption bands if, for instance, the conjugated phenyl click product **4c** is compared to the benzyl derivative **4a**, which further proves that the triazole constitutes an insulating bridging unit between the π -conjugated systems.

Within the 4,4'-substituted series, similar trends can be observed. However, the 4,4'-substituted complexes showed slightly redshifted absorption spectra and higher extinction coefficients compared with their 5-substituted analogues. Hexyl chains at the phenylacetylide units again cause a redshift of the MLCT absorption (e.g. 6a and 6b). A blueshifted absorption is observed after the ethynyl group is clicked with benzyl azide (e.g. 7a and 8a). However, the molar extinction coefficient of the MLCT band is marginally increased with the triazolyl substituents, as opposed to the 5-substituted series. Figure 1c exemplifies the general statement that there is no significant change in the absorption spectra if the benzyl (e.g. 8a) and phenyl (e.g. 8c/8e) click products are compared, which is because of the insulating nature of the triazole linker (vide supra). Furthermore, there is no noticeable shift if the alkyl chains are attached to the clicked phenyl moiety on the bpy ligand (8e). Indeed, the absorption spectra of the complexes are identical as the

chromophoric units of **8a**, **8c** and **8e** can be considered equivalent because of to the lack of interaction through the triazole unit.

Further effects can be observed in the luminescence spectra in deaerated DCM at room temperature and 77 K. At room temperature, all compounds except **9**, which is blueshifted and has a maximum at 577 nm, display broad, unstructured emission bands with maxima ranging from 598–660 nm. In addition, the large Stokes shifts (7136–8115 cm⁻¹) and the excited state liftetimes (66–777 ns) are indicative of ³MLCT excited states. In general, the emission shifts caused by different substitution patterns follow the same trends observed for the MLCT absorption bands (vide supra). However, generally, the emission maxima of the substituted complexes display larger redshifts (609–2180 cm⁻¹) than the corresponding MLCT absorption bands (420–1703 cm⁻¹) compared to **9**.

Figure 2a depicts the emission spectra of 9 and examples of the 5-substituted series, 2a, 4a and 4b, which demonstrate the general trends observed. If an ethynyl-substituted complex (e.g. 2a) is compared with its click product (e.g. 4a), a distinct blueshift is observed, whereas the insertion of hexyl chains (e.g. 4b) causes a redshift. Vibrational progressions and blueshifts are apparent at 77 K (Figure 2b) and the emission profiles become structured. However, the trends mentioned above are still observed. The shifts and vibrational progressions can be explained by the lack of stabilization of the excited ³MLCT states by the frozen solvent, which results in a shift of the ³MLCT state to higher energies compared to fluid solutions. Greater mixing with the close-lying ³IL states can therefore occur, which leads to more structured emissions and longer excited-state lifetimes.

a) 50 9 2a 40 2b ε [10³ M⁻¹ cm⁻¹] 30 20 10 0 400 700 300 500 600 λ [nm] b) 50 3a 4a 40 ε [10³ M⁻¹ cm⁻¹] 30 20 10 0 300 400 500 600 700 λ [nm] C) 70 8a 8c 60 - 8e 50 ε [10³ M⁻¹ cm⁻¹] 40 30 20 10 0 300 400 500 600 700 λ [nm]

Figure 1. Absorption spectra of representative Pt^{II} complexes in DCM ($c \approx 10^{-5} \text{ mol L}^{-1}$) at room temp. (a) Influence of *n*-hexyl chains at the phenylacetylides on the 5-substituted series and comparison with **9**, (b) 5-triazolyl- vs. 5-ethynyl-substituted bpy Pt^{II} complexes, (c) different 4,4'-triazolyl-substituted bpy Pt^{II} derivatives.

At room temperature, the 4,4'-substituted series (Figure 2c) also displays blueshifts upon click functionalization (cf. **6a** and **8a**), whereas hexyl chains at the phenylacetlyide unit (e.g. **8b**) give a redshift, as previously observed for the 5-substituted analogues.

The influence on the emission spectra of different substituents clicked in the 4,4'-position of the bpy Pt^{II} complexes is depicted in Figure 3. For instance, if a benzyl click prod-

uct (e.g. 8a) is compared with the corresponding conjugated phenyl click product (e.g. 8c), only a slight redshift of the MLCT emission band is observed. Thus, the direct linkage of an aromatic moiety to the triazole ring has no significant influence on the lumophoric unit. Nonetheless, although the MLCT absorption maximum of 8c is shifted by only 170 cm^{-1} to lower energies compared with 8a, the emission maximum is shifted by about 429 cm⁻¹. Even though the triazole spacer hinders the delocalization of the bipyridine ligand to the clicked moiety, its effect is more pronounced on the emissive state than on the vertical absorption state. This is confirmed by the blueshifted emission spectrum of 8e (Figure 3) compared with 8c, and can be explained by the electron-donor ability of the hexyl chains. As already discussed for the 5-substituted complexes, for the 4,4'-substituted compounds we also see a larger ³IL character of the emission at 77 K. The effect is more pronounced with substituents that favour a larger ³IL character of the emissive state (e.g. clicked phenyl groups) and by those that destabilize the HOMO (e.g. hexyl groups at the phenylacetvlides). Therefore, blueshifted excitation and emission spectra are observed for 8c and 8d at 77 K compared to 8a and 8b

Within the 5-substituted series, the 77 K emission spectra of 2a and 4a look nearly identical between 500 and 650 nm (Figure 2b). However, an additional emission band at around 750 nm appears in the spectrum of 2a, which is not apparent for 4a and 4b, and vanishes at lower concentrations (Figure S1, Supporting Information). Furthermore, excitation spectra monitored at 77 K at 530 and 740 nm showed nearly identical profiles (Figure S2). Thus, the redshifted band is assigned to an aggregate emission with weak ground-state coupling (excimer emission), which has been previously reported.^[26] In general, the tendency for aggregation seems to be lower for hexyl-substituted phenylacetvlide complexes and 5-substituted click products. For the 4,4'-substituted bpy Pt^{II} acetylide series, the propensity for aggregation seems to be higher. Indeed, in some cases, the intensity of the aggregate luminescence at 77 K is even higher than the corresponding monomer emission (Figure 2d). All the compounds were measured at concentrations of 10^{-5} M and the aggregate emissions at 77 K (if observed) are depicted in the Supporting Information along with their excited state lifetimes, which are generally shorter $(< 1 \mu s)$. No aggregate emission was observed at room temperature, even at concentrations up to 5×10^{-4} m in DCM (e.g. Figure S3).

The photoluminescence quantum yields (Φ), the lifetimes (τ) at room temperature and the derived radiative (k_r) and nonradiative (k_{nr}) decay rate constants are listed in Table 1. A Φ of 0.28 was measured for **9**, which decreases upon insertion of triple bonds in the 5- or 4,4'-postition. The increased k_{nr} value is most likely due to the extended conjugation and additional vibrational states. A further drop is observed after attaching hexyl chains to the phenylacetylide ligands due to a larger density of vibrational states. As a result, k_{nr} is enhanced and Φ is lowered. For the click-functionalized complexes, Φ increases again, ranging from 0.18–



Figure 2. Normalized emission spectra in DCM ($c \approx 10^{-5} \text{ mol L}^{-1}$, $\lambda_{Ex} = 400 \text{ nm}$) of 5-substituted bpy Pt^{II} complexes measured (a) at room temp. and (b) in a DCM glassy matrix at 77 K. 4,4'-Substituted bpy Pt^{II} complexes measured (c) at room temp. and (d) in a DCM glassy matrix measured at 77 K.



Figure 3. Normalized emission spectra of different 4,4'-triazolylsubstituted bpy Pt^{II} compounds in DCM ($c \approx 10^{-5} \text{ mol } \text{L}^{-1}$) at room temp., $\lambda_{\text{Ex}} = 430 \text{ nm}$.

0.33 for products without hexyl chains and from 0.05–0.10 for compounds with hexyl chains on the phenylacetylide ligands. Even though the latter complexes have good solubility, as opposed to their derivatives without alkyl chains, they are also less emissive. Interestingly, **8e**, which bears

hexyl chains at the phenyltriazolyl moiety, has good solubility and a relatively high Φ of 0.25. The alkyl chains attached by the triazole linker do not seem to have an influence on the nonradiative decay rate constant. If the $k_{\rm nr}$ values of **8a**/ **8c/8e** and **4a/4c** are compared, it is clear that they are relatively low, 9×10^5 – 13×10^5 s⁻¹, and they do not change with different substituents at the triazolyl moiety.

Conclusively, click chemistry has been shown to be a suitable method to attach a variety of functional groups to Pt^{II} complexes, such as solubilizing alkyl chains, or to decorate the backbone of target molecules, while precisely controlling the photophysical properties of the lumiphore.

Electrochemistry

Selected complexes have been investigated electrochemically to determine their redox properties and to measure the HOMO/LUMO energy levels of the series. Cyclic voltammetry (CV) was measured in N,N-dimethylformamide (DMF) solution with tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Table 2 summarizes the electrochemical data. The cyclic voltammograms look alike for all complexes. There are two reversible reduction waves at around -1.5 and -2.2 V (vs. Fc/Fc⁺), which correspond to two one-electron reductions of the bpy ligand.^[8k] An irreversible oxidation wave at around 0.9 V corresponds to the PtII/PtIII oxidation, which can be seen in Figure 4a for 8a. The irreversibility is probably due to the reductive elimination of the phenylacetylide ligands as a follow-up reaction after the PtII core is oxidized.[27] Differential pulse voltammograms (DPVs) were recorded to determine standard potentials (Figure 4b). The reductive waves were well resolved, but the irreversibility of the oxidation made the acquisition of well-resolved DPVs challenging. For all complexes, the HOMO levels lie in the range of -5.74 to -5.92 eV vs. vacuum, and the LUMO levels between -3.74 and -3.51 eV, except for 9, which shows a LUMO at -3.46 eV. Hexyl chains at the phenylacetylide ligands seem to have almost no effect on the HOMO/ LUMO levels. After the click reaction (going from ethylene substituents to triazole substituents) the HOMO and especially the LUMO energies increase, which is consistent with the observed blueshifts in the absorption and emission spectra. If the 4,4'-substitution pattern is compared to the 5substitution pattern, one can see that the changes in HOMO/LUMO energies are very small.

Table 2. Electrochemical parameters of selected complexes.

	$\begin{array}{c} E^0{}_{\mathrm{ox}}{}^{[a]}\\ [\mathrm{V}] \end{array}$	$\begin{array}{c} E^0{}_{\mathrm{red1}}{}^{[a]}\\ [\mathrm{V}] \end{array}$	$\begin{array}{c} E^0{}_{\rm red2}{}^{[a]}\\ [V] \end{array}$	$E_{\rm HOMO}^{\rm [b]}$ [eV]	$E_{\rm LUMO}^{\rm [b]}$ [eV]	$E_{\rm g}^{\rm [c]}$ [eV]
2a	0.92	-1.53	-2.22	-5.85	-3.74	2.12
2b	0.87	-1.53	-2.22	-5.84	-3.69	2.15
3a	0.97	-1.53	-2.21	-5.92	-3.67	2.25
4a	0.83	-1.65	-2.28	-5.79	-3.53	2.26
4b	0.86	-1.66	-2.29	-5.83	-3.52	2.31
4c	0.86	-1.62	-2.23	-5.81	-3.56	2.26
4d	0.83	-1.66	-2.28	-5.80	-3.51	2.29
6a	0.94	-1.45	-2.05	-5.90	-3.72	2.18
7a	0.91	-1.48	-2.08	-5.85	-3.63	2.22
7b	1.10	-1.49	-2.11	-5.92	-3.68	2.23
8a	0.81	-1.62	-2.24	-5.79	-3.57	2.22
8c	0.83	-1.63	-2.24	-5.77	-3.55	2.22
8d	0.80	-1.61	-2.21	-5.74	-3.56	2.18
8e	0.87	-1.61	-2.22	-5.81	-3.57	2.22
9	0.91	-1.72	-2.38	-5.88	-3.46	2.43

[a] Measured vs. Fc/Fc⁺ in DMF (0.1 M TBAPF₆), $c = 10^{-3}$ mol L⁻¹, 295 K, scan rate = 100 mV s⁻¹. Potentials were determined using DPV. [b] Vs. vacuum, determined from the onsets of oxidation and reduction waves, using the equation $E_{\text{HOMO/LUMO}} = -5.1 \text{ eV} - E_{\text{ox}}^{\text{onset}/E_{\text{red1}}^{\text{onset}}}$ [c] Calculated by the difference of the values of E_{LUMO} and E_{HOMO} .

The energy gap was calculated by the difference of the HOMO and LUMO energies to be between 2.1 and 2.3 eV for all compounds, whereas the gap for **9** is about 0.2 eV higher (2.43 eV). In general, it can be stated that the actual HOMO/LUMO gaps differ to some extent from the spectroscopic absorptions and emissions, which indicates that they cannot be simply regarded as HOMO–LUMO transitions. The HOMO/LUMO gaps are consistent with the observed photophysical trends, even though the electrochemically measured differences are less pronounced.





Figure 4. (a) Representative CVs and (b) DPVs of **8a** in DMF (0.1 M TBAPF₆), $c = 10^{-3} \text{ mol } \text{L}^{-1}$, scan rate 100 mV s⁻¹.

PLED Fabrication

In order to test the applicability of our clicked Pt^{II} acetylides as triplet emitters in PLEDs, the two brightest derivatives, **4a** and **8a**, were investigated as dopants. The complexes were employed in a solution-processed simple device structure: ITO/PEDOT (35 nm)/PVK:PBD:x wt.-% Pt (60 nm)/TPBI (30 nm)/CsF (1.5 nm)/A1 (80 nm). [ITO = indium tin oxide, PEDOT = poly(3,4-ethylenedioxythiophene), PBD = 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4oxadiazole, TPBI = 1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene, x = 3, 5]. A schematic representation of the device architecture is given in Figure 5.



Figure 5. Schematic representation of the device architecture, EL = PVK:PBD: x wt.-% Pt (x = 3, 5).

FULL PAPER

Table 3. PLED	performances	obtained	with	4a	and	8a	in	PV	ΥK
---------------	--------------	----------	------	----	-----	----	----	----	----

Device	Dopant	Loading [wt%]	$L_{\rm max} [{\rm cd} {\rm m}^{-2}]^{[{\rm a}]}$	$LE [cd A^{-1}]^{[b]}$	$PE \ [\mathrm{lm} \mathrm{W}^{-1}]^{[\mathrm{c}]}$	EQE [%] ^[d]	$V_{\rm on} [V]^{[e]}$	$CIE [x,y]^{[f]}$
1	4a	5	6648	3.3	1.3	0.91	5.6	0.44, 0.55
2	4a	3	9052	3.0	1.7	0.82	4.9	0.43, 0.56
3	8a	3	2408	2.0	0.7	0.55	5.6	0.44, 0.55

[a] Maximum luminance. [b] Light-harvesting efficiency. [c] Power conversion efficiency. [d] External quantum efficiency. [e] Turn-on voltage recorded at 1 cd m^{-2} . [f] Commission International de l'Eclairage coordinates at 11 V.

The films were prepared by spin coating tetrachloroethane solutions, even though the solubility of 8a was relatively low. The highest attainable concentration was 3 wt.-% of 8ain a PVK matrix. Complex 4a was processed at the same concentration for comparison (Table 3). The better solubility of 4a allowed the use of higher dopant concentrations in PVK. The best device was obtained using 5 wt.-% of 4a.

By using this simple device structure, the performances of the spin-coated devices with a maximum power conversion efficiency (*PE*) of 1.7 lmW⁻¹, light-harvesting efficiency (*LE*) of 3.3 cdA⁻¹ and external quantum efficiency (*EQE*) of 0.91% cannot compete with state-of-the-art devices that use Pt^{II} complexes as triplet emitter molecules in vapour-deposited devices.^[1d,1e] However, the energy transfer from the PVK matrix to the Pt^{II} dopant occurred quantitatively as the electroluminescence spectra did not show emission from the PVK host (Figure 6a). The turn-on voltage of the resulting orange emitting devices was measured at 1 cdm⁻² and ranged from 4.9 to 5.6 V, which shows that the charge-transport ability of the Pt^{II} complexes employed is



Figure 6. (a) Electroluminescence spectra and (b) current density/ voltage/brightness plot for Device 1 using 5 wt.-% **4a**.

adequate. The maximum brightness of 6648 and 9052 cd m⁻² for devices with 5 and 3 wt.-% **4a**, respectively, was obtained at voltages of ca. 13 V (Figure 6b). A device with a comparable structure and a related emitter complex [4,4'-dimethyl-bpy Pt^{II} bis(phenylacetylide)] was described in 2001 by Che and coworkers, who reported a maximum luminance of 945 cd m⁻² at 28 V and a maximum power efficiency of 1.33 lm W⁻¹.^[8k] A more recent example of spin-coated OLEDs using Pt^{II} phosphors in an optimized device structure delivered light-harvesting efficiencies of 15.6 cd A⁻¹ and a maximum brightness of 11360 cd m⁻².^[4d] Despite the fact that the our devices can still be improved, they also demonstrate the suitability of the click-decorated complexes for solution-processed PLEDs.

Conclusions

A series of substituted bpy Pt^{II} bisacetylides was synthesized and postfunctionalized with different azides by click chemistry and their photophysical and electrochemical properties were investigated. They showed ³MLCT emission at room temperature with maxima ranging from 598-660 nm and their PLQYs in solution reached 0.33, which shows that click chemistry is an efficient method to functionalize luminescent bpy PtII complexes without diminishing their emissive properties. Several substituents can be introduced in high yields by employing the corresponding azides without affecting the acetylide ligands. If the complexes are linked through a triazole ring to different moieties, only minor influences on k_{nr} were observed despite the fact that slight absorption and emission shifts become apparent. Furthermore, the PLQYs remain unaffected, which is not the case if additional groups, such as solubilizing alkyl chains, are introduced to the phenylacetlyide ligands. Therefore, the CuAAC click reaction, which results in 1,2,3-triazoles as bridging moieties, constitutes a versatile and adequate method for the postfunctionalization of PtII complexes, both from synthetic and photophysical viewpoints. This opens the possibility to covalently link Pt^{II} emitters to surfaces, polymers or other molecular scaffolds, which is the objective of ongoing investigations in our labs.

Experimental Section

Synthesis: 5-(Trimethylsilylethynyl)-2,2'-bipyridine,^[16] 4,4'-bis(trimethylsilylethynyl)-2,2'-bipyridine,^[17] *cis*-dichloro(dimethyl sulfoxide)platinum(II),^[18] phenyl azide,^[22] benzyl azide,^[23] 4-hexylphenyl azide^[24] and 1-ethynyl-4-hexylbenzene^[29] were synthesized according to literature protocols. CODPt(C=CPh)₂^[30] was synthesized



from CODPtCl₂^[31] by analogy to 2a (COD = cyclooctadiene). Potassium tetrachloroplatinate (K₂PtCl₄) was purchased from ABCR and tetrakis(acetonitrile)copper(I) hexafluorophosphate [Cu(CH₃CN)₄PF₆] was purchased from Aldrich. 2,2'-Bipyridine, phenylacetylene and all solvents were purchased from Merck (VWR International) and were used as received for workup procedures, distilled for purification purposes and dried for use in reactions according to standard protocols.^[32] Column chromatography was performed with flash silica gel, particle size 0.04-0.064 mm, from Macherey-Nagel and basic aluminium oxide (alumina) "90" (particle size 0.04-0.064 mm) from Merck, respectively. The alumina was deactivated to "Brockmann" activity II-III by adding 5% distilled water. TLC was carried out on aluminium sheets coated with silica gel (Merck TLC Silica gel 60 F₂₅₄) and aluminium oxide (Merck TLC Aluminium oxide 150 F254, neutral).

Physicochemical, Electrochemical and Photophysical Measurements: NMR spectra were recorded with a Bruker 400 spectrometer at 25 °C, unless noted otherwise. 500 MHz spectra were recorded with a Bruker 500 spectrometer. Chemical shifts (δ) are expressed in ppm using residual solvent protons (CDCl₃: $\delta^{^{1}H} = 7.26$ and $\delta^{^{1}C} = 77.36$ ppm; CD₂Cl₂: $\delta^{^{1}H} = 5.33$ and $\delta^{^{13}C} = 54.24$ ppm; [D₆]DMSO: $\delta^{^{1}H} = 2.54$ and $\delta^{^{13}C} = 40.45$ ppm)^[33] as internal standards. Occasionally, attached proton test (APT) spectra were measured for the specific evaluation of the ¹³C NMR spectra. The numbering of atoms for the assignment of NMR signals was chosen for practical considerations and does not conform to IUPAC nomenclature. MALDI-TOF MS were measured with a Bruker Daltonics Reflex III and HRMS were measured with a micrOTOF-Q43 apparatus and ESI source at the University of Stuttgart and with a Bruker solariX spectrometer and MALDI or ESI source at Ulm University. Melting points were determined with a Büchi B-545 apparatus. Elemental analyses were performed with an Elementar Vario EL. Optical measurements were carried out in 1-cm cuvettes with Merck spectroscopic grade solvents. Absorption spectra were recorded with a Perkin-Elmer Lambda 19 spectrometer. Steady-state luminescence experiments were performed with a Spex FluoroLog-3 spectrofluorometer (Horiba-Jobin-Yvon Inc.) equipped with a TBX detector and double excitation and emission monochromators. The emission spectra were corrected for monochromator and detector efficiency and for the source intensity (450 W xenon lamp). Time-resolved measurements were performed using the time-correlated single-photon counting option with the Spex FluoroLog-3 instrument. A NanoLED [431 nm; full width half maximum (FWHM) < 200 ps] with repetition rates between 10 kHz and 1 MHz was used to excite the samples. The excitation sources were mounted directly on the sample chamber at 90° to a double grating emission monochromator (2.1 nm/mm dispersion; 1200 grooves/ mm) and collected by a TBX-4-X single-photon-counting detector. The photons collected at the detector were correlated by a time-toamplitude converter to the S3 excitation pulse. Signals were collected using an IBH DataStation Hub photon counting module and data analysis was performed using the commercially available DAS6 software (Horiba-Jobin-Yvon Inc.). The quality of 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 (excitation wavelengths: 250-700 nm; bandwidth: FWHM 10 nm), C7473 photonic multichannel analyzer, integrating sphere and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka). The detector was a PMA multichannel capable of simultaneously measuring multiple wavelengths that have

been corrected for wavelength sensitivity. IR spectra was measured with a Perkin–Elmer FTIR Spectrum 2000. CV experiments were performed with a computer-controlled Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. All potentials were internally referenced to the Fc/Fc⁺ couple.

PLED Fabrication: The light-emitting devices were fabricated using the structure ITO/PEDOT:PSS (35 nm)/emitting layer (60-80 nm)/ TPBI (30 nm)/CsF (1.5 nm)/Al (80 nm), in which PEDOT:PSS is poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene). The ITO glass substrate was treated for 10 min with UV/O₃ (UVO Cleaner 144AX, Jelight Company) before further processing. The PEDOT:PSS was spin-coated directly onto ITO substrate, using a spincoater P6700 (Specialty Coating Systems) and then dried at 100 °C for 10 min. The emitting layer, containing a PVK host polymer blended with 30 wt.-% of PBD and 3-5 wt.-% of platinum(II) complex, was spin-coated on top of the PEDOT:PSS layer using tetrachloroethane as solvent. The sample was then dried for 90 min at 50 °C. Prior to film casting, the polymer solution was filtered through a Teflon filter (0.45 µm). The TPBI layer was grown through thermal sublimation in a vacuum of 3×10^{-6} mbar using an MBraun evaporation chamber. The cathode was completed through thermal deposition of CsF (1.5 nm)/Al (80 nm). All measurements were conducted inside a glove box under an inert atmosphere. The electroluminescent device was characterized by attaching a computer-controlled low-noise single-channel direct-current power source that can act as both voltage source and current source, and a voltage meter or current meter (Keithley 2600, Keithley Instruments). Light from the diode was coupled to a photodiode and read by an electrometer/high-resistance meter (Keithley 6517, Keithley Instruments). The data output was managed by a Labview-based program (National Instruments). Calibration of the photodiode was performed at a fixed current with a luminance meter (LS-100 Minolta). For every diode with a different spectral distribution of light, the photocurrent as measured by the photodiode was correlated to the light output in candles per square meter by this calibration. When recording an electroluminscence spectrum, a fibreoptic-coupled spectrometer (USB2000, Ocean Optics) was used. The emission was corrected for the wavelength dependence of the spectrometer.

Dichloro[5-(trimethylsilylethynyl)-2,2'-bipyridine]platinum(II) (1):^[19] (DMSO)₂PtCl₂ (0.242 g, 0.573 mmol) and 5-(trimethylsilylethynyl)-2,2'-bipyridine (0.145 g, 0.573 mmol) were dissolved in acetonitrile (25 mL) and stirring was continued at room temp. overnight. The solvent was removed in vacuo, and the residue was suspended in diethyl ether, filtered and washed with diethyl ether. The solid was dried in vacuo, and 1 (0.249 g, 0.48 mmol, 84%) remained as an orange powder. $R_{\rm f} = 0.29$ (alumina, DCM). ¹H NMR (400 MHz, CD_2Cl_2 : $\delta = 0.31$ (s, 9 H, 3 × CH_3), 7.60–7.64 (m, 1 H, H-5'), 7.98 (d, ${}^{3}J = 8.4$ Hz, 1 H, H-3), 8.02 (d, ${}^{3}J = 7.8$ Hz, 1 H, H-3'), 8.19 (dd, ${}^{4}J = 1.8$ Hz, ${}^{3}J = 8.4$ Hz, 1 H, H-4), 8.21 (td, ${}^{4}J = 1.4$ Hz, 1 H, ${}^{3}J$ = 7.9 Hz, H-4'), 9.65 (d, ${}^{4}J$ = 1.8 Hz, 1 H, H-6), 9.66 (dd, ${}^{4}J$ = 1.1 Hz, ${}^{3}J$ = 5.9 Hz, 1 H, H-6') ppm. ${}^{13}C$ NMR (100 MHz, CD_2Cl_2): $\delta = 0.0 (3 \times CH_3)$, 99.0 (C=*C*-TMS), 105.8 (C=*C*-bpy), 123.3 (C-3), 124.1 (C-3'), 124.8 (C-5), 128.1 (C-5'), 140.3 (C-4), 142.4 (C-4'), 150.2 (C-6), 152.4 (C-6'), 156.3 (C-2), 157.1 (C-2') ppm. IR (KBr): $\tilde{v} = 3048$ (m), 2959 (w), 2162 (w), 1604 (w), 1468 (s), 1442 (m), 1376 (m), 1249 (m), 1235 (m), 882 (s), 845 (s) cm⁻¹. MS (MALDI-TOF, dithranol): *m*/*z* = 481 [M - Cl]⁺, 962 [2 M - 2 Cl]⁺, 998 [2 M – Cl]⁺.

Bis(phenylethynyl)[5-(trimethylsilylethynyl)-2,2'-bipyridine]platinum(II) (2a):^[81] Compound 1 (0.10 g, 0.193 mmol) was dissolved in DCM (10 mL) and diisopropylamine (0.5 mL) under argon. The solution was degassed, and CuI (4 mg, 0.021 mmol) and phenylacetylene (0.085 mL, 0.772 mmol, 0.079 g) were added. Stirring at room temp. was continued overnight. The solvent was removed in vacuo, and the crude product was purified by column chromatography using alumina and petroleum ether (PE)/DCM (1:5). Product 2a (122 mg, 0.188 mmol, 97%) was obtained as an orange powder. $R_{\rm f} = 0.50$ (alumina, PE/DCM, 1:5). ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.32$ (s, 9 H, 3×CH₃), 7.19–7.23 (m, 2 H, H-6''), 7.29–7.33 (m, 4 H, H-5''), 7.50–7.52 (m, 4 H, H-4''), 7.59–7.63 (m, 1 H, H-5'), 8.09–8.18 (m, 4 H, H-3,3', 4,4'), 9.68 (d, ${}^{3}J$ = 5.5 Hz, 1 H, H-6'), 9.77 (d, ${}^{4}J$ = 1.7 Hz, 1 H, H-6) ppm. ${}^{13}C$ NMR (100 MHz, CD_2Cl_2 : $\delta = 0.2 (3 \times CH_3), 87.8 + 88.6 (C-2''), 100.1 (2 \times C \equiv C-C)$ TMS), 102.6 (C-1''), 104.5 ($2 \times C \equiv C$ -bpy), 123.9 (C-3'), 124.5 (C-3), 124.6 (C-5), 126.5 + 126.6 (C-3''), 128.2 (C-5'), 128.8 + 128.9 (C-5^{''}, C-6^{''}), 132.5 + 132.6 (C-4^{''}), 139.6 (C-4[']), 141.8 (C-4), 151.7 (C-6'), 154.1 (C-6), 155.6 (C-2'), 156.4 (C-2) ppm. IR (KBr): $\tilde{v} =$ 3073 (w), 3049 (m), 3023 (w), 2958 (m), 2166 (w), 2126 (s), 2115 (s), 1635 (w), 1592 (m), 1485 (s), 1468 (m), 1249 (m), 1237 (m), $1217 \text{ (m)}, 1067 \text{ (m)}, 1025 \text{ (m)}, 878 \text{ (s)}, 844 \text{ (s)}, 754 \text{ (s)}, 692 \text{ (s)} \text{ cm}^{-1}.$ MS (MALDI-TOF, dithranol): $m/z = 649 \text{ [M]}^+$, 1298 [2 M]⁺. C31H26N2PtSi (649.74): calcd. C 57.31, H 4.03, N 4.31; found C 56.93, H 4.17, N 4.16.

Bis(4-hexylphenylethynyl)[5-(trimethylsilylethynyl)-2,2'-bipyridine]platinum(II) (2b): Compound 1 (0.30 g, 0.579 mmol) was dissolved in DCM (60 mL), and diisopropylamine (4 mL) was added. The solution was degassed, and CuI (10 mg, 0.060 mmol) and 1-ethynyl-4-hexylbenzene (0.324 g, 1.736 mmol) were added. Stirring was continued at room temp. overnight. The solvent was removed in vacuo, and the residue was purified by column chromatography with alumina and DCM/PE (5:4). Product 2b (0.426 g, 0.521 mmol, 90%) remained as a red-brown solid. $R_{\rm f} = 0.36$ (alumina, DCM/ PE, 5:4). ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.34$ (s, 9 H, 3×CH₃), 0.90-0.94 (m, 6 H, H-12''), 1.36-1.42 (m, 12 H, H-11'', H-10'', H-9"), 1.61-1.69 (m, 4 H, H-8"), 2.62-2.66 (m, 4 H, H-7"), 7.14 (d, ${}^{3}J = 8.1 \text{ Hz}, 4 \text{ H}, \text{H-5''}, 7.37 + 7.40 (2 \times \text{d}, {}^{3}J = 8.1 \text{ Hz}, 2 \times 2 \text{ H},$ H-4''), 7.43–7.47 (m, 1 H, H-5'), 7.97 (td, ${}^{4}J$ = 1.5 Hz, ${}^{3}J$ = 7.8 Hz, 1 H, H-4'), 8.08 (dd, ${}^{4}J$ = 1.9 Hz, ${}^{3}J$ = 8.3 Hz, 1 H, H-3'), 8.13– 8.18 (m, 2 H, H-3, H-4), 9.37 (d, ${}^{4}J$ = 1.6 Hz, 1 H, H-6), 9.43 (dd, ${}^{4}J$ = 1.0 Hz, ${}^{3}J$ = 5.5 Hz, 1 H, H-6') ppm. ${}^{13}C$ NMR (100 MHz, CD₂Cl₂): $\delta = 0.2 (3 \times CH_3)$, 14.7 (C-12''), 23.6 (C-11''), 29.8 (C-10''), 32.2 (C-9''), 32.5 (C-8''), 36.5 (C-7''), 87.0 + 87.9 (C-2''), 100.2 (C≡C-TMS), 102.4 (C-1''), 104.0 (C≡C-bpy), 124.1 (C-5), 124.4 (C-3'), 125.0 (C-3), 126.0 (C-3''), 127.9 (C-5'), 128.9 (C-5''), 132.3 + 132.3 (C-4''), 139.4 (C-4'), 141.4 + 141.5 (C-6''), 141.8 (C-4), 151.2 (C-6'), 153.5 (C-6), 155.5 (C-2'), 156.1 (C-2) ppm. IR (KBr): $\tilde{v} = 2956$ (m), 2926 (s), 2854 (m), 2167 (w), 2113 (m), 1637 (w), 1604 (m), 1504 (m), 1467 (m), 1440 (w), 1376 (w), 1249 (m), 1236 (w), 878 (m), 844 (s) cm⁻¹. MS (MALDI-TOF, dithranol): m/z = 818 $[M]^+$, 1634 $[2 M]^+$. C₄₃H₅₀N₂PtSi (818.06): calcd. C 63.13, H 6.16, N 3.42; found C 63.11, H 6.15, N 3.37.

(5-Ethynyl-2,2'-bipyridine)bis(phenylethynyl)platinum(II) (3a): Complex 2a (90 mg, 0.139 mmol) was dissolved in DCM (15 mL), and KF (12 mg, 0.208 mmol) and methanol (2 mL) were added. Stirring was continued at room temp. The solvent was removed in vacuo, and the residue was purified by column chromatography with alumina and PE/DCM (1:5) and 100% DCM. Product 3a (75 mg, 0.13 mmol, 94%) remained as a red-brown powder. $R_f =$ 0.16 (alumina, PE/DCM, 1:5). ¹H NMR (400 MHz, CD₂Cl₂): $\delta =$ 3.59 (s, 1 H, C=CH), 7.19–7.24 (m, 2 H, H-6''), 7.29–7.24 (m, 4 H, H-5''), 7.48–7.51 (m, 4 H, H-4''), 7.58–7.64 (m, 1 H, H-5'), 8.12–8.16 (m, 3 H, H-4,4', 3), 8.22 (dd, ⁴J = 1.9 Hz, ³J = 8.4 Hz, 1 H, H-3'), 9.66 (d, ³J = 5.5 Hz, 1 H, H-6'), 9.74 (d, ⁴J = 1.5 Hz, 1 H, H-6) ppm. ¹³C NMR (100 MHz, CD₂Cl₂): δ = 78.9 (C=*C*-bpy), 85.8 (C-2''), 100.8 (C=*C*-H), 102.6 + 102.7 (C-1''), 123.4 (C-3'), 123.8 (C-5), 124.2 (C-3), 126.5 (C-3''), 128.5 (C-5'), 128.7 + 128.8 (C-5'', C-6''), 132.5 (C-4''), 139.8 (C-4'), 142.4 (C-4), 151.9 (C-6'), 154.5 (C-6), 156.2 (C-2,2') ppm. IR (KBr): \tilde{v} = 3215 (s), 2124 (m), 2112 (s), 1592 (m), 1485 (s), 1466 (m), 1440 (m), 784 (m), 758 (s), 694 (m) cm⁻¹. MS (MALDI-TOF, dithranol): *m*/*z* = 577 [M]⁺, 1154 [2 M]⁺. C₂₈H₁₈N₂Pt (577.55): calcd. C 58.23, H 3.14, N 4.85; found C 57.97, H 3.26, N 4.78.

(5-Ethynyl-2,2'-bipyridine)bis(4-hexylphenylethynyl)platinum(II) (3b): Complex 2b (74.7 mg, 0.091 mmol) was dissolved in DCM (15 mL) and methanol (2 mL). KF (8 mg, 0.137 mmol) was added, and stirring was continued at room temp. overnight. The solvent was removed in vacuo, and the residue was purified by column chromatography with alumina and PE/DCM (1:2). Product 3b (67 mg, 0.090 mmol, 99%) was obtained as an orange powder. $R_{\rm f}$ = 0.38 (alumina, DCM/PE, 2:1). ¹H NMR (400 MHz, CD₂Cl₂): δ = 0.91 (t, ${}^{3}J = 6.8$ Hz, 6 H, H-12''), 1.31–1.39 (m, 12 H, H-11'', H-10^{''}, H-9^{''}), 1.60–1.68 (m, 4 H, H-8^{''}), 2.62 (t, ${}^{3}J$ = 7.7 Hz, 4 H, H-7''), 3.58 (s, 1 H, C=CH), 7.14 (dd, ${}^{4}J$ = 3.1 Hz, ${}^{3}J$ = 8.1 Hz, 4 H, H-5''), 7.40 (dd, ${}^{4}J$ = 3.1 Hz, ${}^{3}J$ = 8.1 Hz, 4 H, H-4''), 7.56– 7.60 (m, 1 H, H-5'), 8.10-8.16 (m, 3 H, H-4,4' H-3), 8.20 (dd, ⁴J = 1.9 Hz, ${}^{3}J$ = 8.4 Hz, 1 H, H-3') 9.64 (d, ${}^{3}J$ = 5.7 Hz, 1 H, H-6'), 9.72 (d, ${}^{4}J$ = 1.7 Hz, 1 H, H-6) ppm. ${}^{13}C$ NMR (100 MHz, CD_2Cl_2): $\delta = 14.7$ (C-12''), 23.5 (C-11''), 29.9 (C-10''), 32.3 (C-9''), 32.6 (C-8''), 36.6 (C-7''), 79.1 (C=C-bpy), 85.7 (C=C-H), 86.0 + 86.7 (C-2''), 102.6 + 102.7 (C-1''), 123.6 (C-3'), 123.7 (C-5), 124.4 (C-3), 126.0 (C-3''), 128.4 (C-5'), 128.9 (C-5''), 132.4 (C-4''), 139.7 (C-4'), 141.6 (C-6''), 142.4 (C-4), 151.9 (C-6'), 154.4 (C-6), 156.3 (C-2,2') ppm. IR (KBr): $\tilde{v} = 2955$ (m), 2926 (s), 2854 (m), 2113 (m), 1636 (s, br), 1504 (m), 1467 (m), 825 (m), 781 (m) cm⁻¹. MS (MALDI-TOF, dithranol): $m/z = 745 \text{ [M]}^+$, 1490 [2 M]⁺. C₄₀H₄₂N₂Pt (745.88): calcd. C 64.41, H 5.68, N 3.76; found C 64.32, H 5.74, N 3.73.

[5-(1-Benzyl-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine]bis(phenylethynyl)platinum(II) (4a): Complex 2a (30 mg, 0.046 mmol) was dissolved in DCM (8 mL) and methanol (2 mL), and KF (4 mg, 0.069 mmol) was added under argon. The solution was degassed, and Cu(CH₃CN)₄PF₆ (3.4 mg, 0.009 mmol), DIPEA (0.02 mL, 0.092 mmol, 11.9 mg), elemental copper (1 mg, 0.009 mmol) and benzyl azide (9.3 mg, 0.069 mmol) were added. Stirring at room temp. was continued for 4 d. 25% ammonia (5 mL) in water (15 mL) and DCM (50 mL) were added. After stirring the solution vigorously for some minutes, the layers were separated, and the aqueous layer was extracted with DCM (30 mL). The organic layer was washed with 0.1 M Na₂/ethylenediaminetetraacetic acid (EDTA) solution and dried with Na2SO4. The solvent was removed in vacuo, and the residue was purified by column chromatography with silica and DCM/diethyl ether (10:1). The product was dissolved in DCM and PE was added to precipitate the solid, which was collected by filtration, washed with PE and dried in vacuo. Product 2a (30 mg, 0.042 mmol, 91%) remained as an orange powder. $R_f = 0.21$ (silica, DCM/diethyl ether, 10:1). ¹H NMR (500 MHz, [D₆]DMSO, 375 K): δ = 5.75 (s, 2 H, H-benzyl), 7.20– 7.23 (m, 2 H, H-6''), 7.30–7.34 (m, 4 H, H-5''), 7.40–7.44 (m, 7 H, H-m,p-Ph, H-4''), 7.50-7.51 (m, 2 H, H-o-Ph), 7.86-7.89 (m, 1 H, H-5'), 8.39 (td, ${}^{4}J$ = 1.5 Hz, ${}^{3}J$ = 7.9 Hz, 1 H, H-4'), 8.62 (d, ${}^{3}J$ = 8.1 Hz, 1 H, H-3'), 8.66 (d, ${}^{3}J$ = 8.4 Hz, 1 H, H-3), 8.71 (s, 1 H, H-5'''), 8.72 (dd, ${}^{4}J$ = 2.0 Hz, ${}^{3}J$ = 8.3 Hz, 1 H, H-4), 9.65 (dd, ${}^{4}J$ = 0.9 Hz, ${}^{3}J$ = 5.5 Hz, 1 H, H-6'), 10.32 (d, ${}^{4}J$ = 1.7 Hz, 1 H, H-6) ppm. ¹³C NMR (125 MHz, [D₆]DMSO, 375 K): δ = 54.0 (Cbenzyl), 89.3 (C-2''), 101.6 (C-1''), 124.0 (C-5'''), 124.2 (C-3), 124.5 (C-3'), 125.6 (C-4), 128.2 (C-5'), 128.3 + 128.4 (C-5''), 128.4 (C-o-Ph), 128.7 (C-p-Ph), 128.8 (C-3''), 129.2 (C-m-Ph), 130.0 (Cq-Ph), 131.7 + 131.9 (C-4''), 135.8 (C-5), 136.0 (C-4'), 140.1 (C-6''), 142.7 (C-4'''), 147.3 (C-6'), 150.5 (C-6), 155.2 (C-2'), 156.3 (C-2) ppm. IR (KBr): $\tilde{v} = 3070$ (m), 3047 (m), 2927 (w), 2111 (s), 1633 (m), 1605 (m), 1592 (m), 1486 (s), 1468 (m), 1456 (m), 1440 (m), 1043 (m), 784 (m), 756 (s), 726 (m), 694 (s) cm⁻¹. MS (MALDI-TOF, dithranol): m/z = 710 [M]⁺, 1420 [2 M]⁺. C₃₅H₂₅N₅Pt (710.71): calcd. C 59.15, H 3.55, N 9.85; found C 58.93, H 3.60, N 9.42.

[5-(1-Benzyl-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine]bis(4-hexylphenylethynyl)platinum(II) (4b): Complex 2b (84.7 mg, 0.104 mmol) was dissolved in DCM (24 mL) and methanol (6 mL) under argon. KF (9 mg, 0.155 mmol), Cu(CH₃CN)₄PF₆ (8 mg, 0.021 mmol), benzyl azide (21 mg, 0.155 mmol), elemental copper (1 mg, 0.021 mmol) and DIPEA (0.04 mL, 0.207 mmol, 27 mg) were added. The synthesis was carried out as described above for compound 4a. The product was purified by column chromatography with basic alumina and DCM. Product 4b (86.3 mg, 0.10 mmol, 95%) was obtained as a red-brown solid. $R_{\rm f} = 0.27$ (alumina, DCM/PE, 2:1). ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.90-0.94$ (m, 6 H, H-12''), 1.33-1.42 (m, 12 H, H-9", H-10", H-11"), 1.61-1.70 (m, 4 H, H-8"), 2.62-2.65 (m, 4 H, H-7"), 5.50 (s, 2 H, H-benzyl), 7.12-7.15 $(2 \times d, {}^{3}J = 8.2 \text{ Hz}, 2 \times 2 \text{ H}, \text{H-5''}), 7.25-7.27 \text{ (m, 2 H, H-o-Ph)},$ 7.35–7.39 (m, 4 H, H-5', H-*m*,*p*-Ph), 7.40 + 7.45 ($2 \times d$, ${}^{3}J$ = 8.1 Hz, 2×2 H, H-4''), 7.89 (s, 1 H, H-5'''), 7.98 (td, ${}^{4}J = 1.5$ Hz, ${}^{3}J =$ 7.8 Hz, 1 H, H-4'), 8.03 (d, ${}^{3}J = 7.8$ Hz, 1 H, H-3'), 8.10 (d, ${}^{3}J =$ 8.4 Hz, 1 H, H-3), 8.48 (dd, ${}^{4}J$ = 2.0 Hz, ${}^{3}J$ = 8.4 Hz, 1 H, H-4), 9.50 (dd, ${}^{4}J = 0.8$ Hz, ${}^{3}J = 5.5$ Hz, 1 H, H-6'), 9.90 (d, ${}^{4}J = 1.9$ Hz, 1 H, H-6) ppm. ¹³C NMR (100 MHz, CD₂Cl₂): δ = 14.7 (C-12''), 23.5 (C-11''), 29.9 + 30.0 (C-10''), 32.3 + 32.4 (C-9''), 32.6 (C-8''), 36.6 + 36.7 (C-7''), 55.2 (C-benzyl), 86.9 + 88.0 (C-2''), 102.6 (C-1''), 122.9 (C-3), 123.8 (C-5'''), 124.4 (C-3'), 126.2 (C-3''), 127.6 (C-5'), 128.9 (C-5''), 129.0 (C-o-Ph), 129.6 (C-p-Ph), 130.0 (C-m-Ph), 131.2 (C-q-Ph), 132.4 + 132.6 (C-4''), 135.5 (C-5), 135.7 (C-4), 139.4 (C-4'), 141.5 (C-6''), 143.5 (C-4'''), 148.3 (C-6'), 151.4 (C-6), 155.2 (C-2), 156.7 (C-2') ppm. IR (KBr): \tilde{v} = 2955 (m), 2927 (s), 2854 (m), 2113 (m), 1635 (m), 1606 (m), 1504 (m), 1466 (m), 826 (w), 725 (m) cm⁻¹. MS (MALDI-TOF, dithranol): m/z = 879[M]⁺, 1758 [2 M]⁺. C₄₇H₄₉N₅Pt (879.03): calcd. C 64.22, H 5.62, N 7.97; found C 63.98, H 5.63, N 7.93.

Bis(phenylethynyl)[5-(1-phenyl-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine]platinum(II) (4c): Complex 2a (58 mg, 0.089 mmol) was dissolved in DCM (24 mL) and methanol (6 mL), and KF (8 mg, 0.13 mmol) was added under argon. The solution was degassed and Cu(CH₃CN)₄PF₆ (7 mg, 0.018 mmol), DIPEA (0.03 mL, 0.18 mmol, 23 mg), elemental copper (1 mg, 0.018 mmol) and phenyl azide (16 mg, 0.13 mmol) were added. Stirring was continued at room temp. for 3 d. Workup and purification were carried out by analogy to 4a. Product 4c (60 mg, 0.086 mmol, 97%) was obtained as a yellow powder. $R_{\rm f} = 0.34$ (silica, DCM/diethyl ether, 20:1). ¹H NMR (500 MHz, [D₆]DMSO, 375 K): δ = 7.20–7.22 (m, 2 H, H-6''), 7.31–7.34 (m, 4 H, H-5''), 7.42 + 7.54 (2×d, ${}^{3}J$ = 7.9 Hz, 2×2 H, H-4"), 7.58–7.61 (m, 1 H, H-p-Ph), 7.67–7.70 (m, 2 H, H-m-Ph), 7.86-7.90 (m, 1 H, H-5'), 7.92-7.93 (m, 2 H, H-o-Ph), 8.38-8.40 (m, 1 H, H-4'), 8.60-8.61 (m, 1 H, H-3'), 8.67-8.69 (m, 1 H, H-3), 8.78-8.80 (m, 1 H, H-4), 9.23 (s, 1 H, H-5""), 9.62-9.65 (m, 1 H, H-6'), 10.40-10.42 (m, 1 H, H-6) ppm. IR (KBr): v = 3069 (w), 3052 (w), 3025 (w), 2926 (w), 2112 (s), 1635 (m), 1596 (s), 1505 (m), 1487 (m), 1467 (m), 1441 (w), 1249 (w), 1070 (w), 1053 (w), 1035 (m), 785 (m), 757 (s), 693 (s) cm⁻¹. MS (MALDI-TOF, dithranol): $m/z = 696 [M]^+$, 1393 [2 M]⁺. C₃₄H₂₃N₅Pt (696.68): calcd. C 58.62, H 3.33, N 10.05; found C 58.53, H 3.35, N 9.90.



Bis(4-hexylphenylethynyl)[5-(1-phenyl-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine|platinum(II) (4d): Complex 2b (63 mg, 0.077 mmol) was dissolved in DCM (24 mL) and methanol (6 mL) under argon. KF (7 mg, 0.116 mmol), Cu(CH₃CN)₄PF₆ (6 mg, 0.015 mmol), phenyl azide (14 mg, 0.116 mmol), elemental copper (1 mg, 0.015 mmol) and DIPEA (0.03 mL, 0.154 mmol, 20 mg) were added. The synthesis and purification were carried out as described above for 4a. Product 4d (58 mg, 0.067 mmol, 87%) was obtained as a red-brown solid. $R_{\rm f} = 0.41$ (silica, DCM/diethyl ether, 20:1). ¹H NMR $(400 \text{ MHz}, \text{CD}_2\text{Cl}_2): \delta = 0.92-0.95 \text{ (m, 6 H, H-12'')}, 1.36-1.43 \text{ (m, })$ 12 H, H-9", H-10", H-11"), 1.61–1.70 (m, 4 H, H-8"), 2.61–2.67 (m, 4 H, H-7''), 7.14–7.16 (m, 4 H, H-5''), 7.24–7.28 (m, 1 H, H-5'), 7.38 + 7.53 (2×d, ${}^{3}J$ = 8.1 Hz, 2×2 H, H-4''), 7.44–7.46 (m, 3 H, H-m, p-Ph), 7.69-7.71 (m, 2 H, H-o-Ph), 7.95-8.00 (m, 2 H, H-3',4'), 8.09 (d, ${}^{3}J$ = 8.4 Hz, 1 H, H-3), 8.39 (s, 1 H, H-5'''), 8.63 $(dd, {}^{4}J = 2.0 \text{ Hz}, 1 \text{ H}, {}^{3}J = 8.3 \text{ Hz}, \text{H-4}), 9.28 (d, {}^{3}J = 5.3 \text{ Hz}, 1 \text{ H},$ H-6'), 9.91 (d, ${}^{4}J$ = 1.8 Hz, 1 H, H-6) ppm. ${}^{13}C$ NMR (100 MHz, CD_2Cl_2): $\delta = 14.7 (C-12'')$, 23.5 (C-11''), 29.9 + 30.0 (C-10''), 32.3 (C-9''), 32.6 (C-8''), 36.6 + 36.7 (C-7''), 87.3 + 88.5 (C-2''), 102.5 + 102.6 (C-1''), 120.9 (C-3), 121.0 (C-o-Ph), 124.0 (C-5''), 124.6 (C-3'), 126.2 + 126.3 (C-3''), 127.2 (C-5'), 128.9 + 129.0 (C-5''), 129.6 (C-q-Ph), 130.4 (C-p-Ph), 130.5 (C-m-Ph), 132.3 + 132.7 (C-4''), 136.4 (C-5), 137.2 (C-4), 139.2 (C-4'), 141.5 (C-6''), 143.7 (C-4'''), 147.7 (C-6'), 150.8 (C-6), 155.1 (C-2'), 156.6 (C-2) ppm. IR (KBr): $\tilde{v} = 2954$ (m), 2926 (s), 2854 (m), 2112 (m), 1636 (s), 1602 (m), 1504 (s), 1466 (m), 825 (w), 757 (m) cm⁻¹. MS (MALDI-TOF, dithranol): $m/z = 863 [M]^+$, 1728 [2 M]⁺. C₄₆H₄₇N₅Pt (865.00): calcd. C 63.87, H 5.48, N 8.10; found C 63.79, H 5.54, N 8.03.

Dichloro[4,4'-bis(trimethylsilylethynyl)-2,2'-bipyridine]platinum(II) (5): (DMSO)₂PtCl₂ (0.279 g, 0.66 mmol) and 4,4'-bis(trimethylsilylethynyl)-2,2'-bipyridine (0.230 g, 0.66 mmol) were dissolved in acetonitrile (25 mL). The yellow solution was stirred at room temp. overnight. The solvent was removed in vacuo, and the residue was suspended in diethyl ether, filtered and washed with diethyl ether. The solid was dried in vacuo, and 5 (0.316 g, 0.515 mmol, 78%) remained as a yellow powder. $R_f = 0.56$ (alumina, DCM). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.31$ (s, 18 H, $6 \times CH_3$), 7.51 (dd, ${}^{4}J =$ 1.5 Hz, ${}^{3}J$ = 6.1 Hz, 2 H, H-5,5'), 7.93 (d, ${}^{4}J$ = 1.5 Hz, 2 H, H-3,3'), 9.66 (d, ${}^{3}J$ = 6.1 Hz, 2 H, H-6,6') ppm. ${}^{13}C$ NMR (100 MHz, CDCl₃): $\delta = -0.2 \ (6 \times CH_3), \ 100.3 \ (2 \times C \equiv C - TMS), \ 108.1$ $(2 \times C \equiv C$ -bpy), 125.3 (C-5,5'), 129.5 (C-3,3'), 135.1 (C-4,4'), 149.5 (C-6,6'), 156.7 (C-2,2') ppm. IR (KBr): $\tilde{v} = 3056$ (w), 2958 (m), 2897 (w), 2111 (m), 1611 (s), 1531 (m), 1479 (m), 1418 (m), 1250 (m), 1228 (m), 950 (m), 868 (s), 845 (s) $cm^{-1}.$ MS (MALDI-TOF, dithranol): $m/z = 577 [M - C1]^+$, 1190 [2 M - C1]⁺. C₂₀H₂₄Cl₂N₂PtSi₂ (614.59): calcd. C 39.09, H 3.94, N 4.56; found C 39.28, H 3.94, N 4.48.

Bis(phenylethynyl)[4,4'-bis(trimethylsilylethynyl)-2,2'-bipyridine]platinum(II) (6a): Compound 5 (0.15 g, 0.244 mmol) was dissolved in DCM (10 mL) and diisopropylamine (8 mL) under argon. The solution was degassed, and CuI (5 mg, 0.027 mmol) and phenylacetylene (0.11 mL, 0.976 mmol, 0.100 g) were added. Stirring was continued at room temp. overnight. The solvent was removed in vacuo, and the residue was purified by column chromatography using alumina and PE/DCM (2:1 and 1:1). Product 6a (132 mg, 0.177 mmol, 73%) was isolated as a red-brown powder. $R_{\rm f} = 0.38$ (alumina, PE/DCM, 1:1). ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.33$ (s, 18 H, 6×CH₃), 7.17-7.21 (m, 2 H, H-6"), 7.27-7.31 (m, 4 H, H-5^{''}), 7.46–7.49 (m, 4 H, H-4^{''}), 7.60 (dd, ${}^{4}J$ = 1.6 Hz, 2 H, ${}^{3}J$ = 5.8 Hz, 5,5'-H), 8.07 (d, ${}^{4}J$ = 1.2 Hz, 2 H, H-3,3'), 9.72 (d, ${}^{3}J$ = 5.8 Hz, 2 H, H-6,6') ppm. ¹³C NMR (100 MHz, CD_2Cl_2): $\delta = -0.1$ $(6 \times CH_3)$, 87.2 (C-2''), 101.3 (2 × C=C-TMS), 103.1 (C-1''), 107.1 $(2 \times C \equiv C$ -bpy), 125.7 (C-5,5'), 126.5 (C-3''), 128.7 (C-5'',6''), 130.4 (C-3,3'), 132.6 (C-4''), 134.6 (C-4,4'), 151.9 (C-6,6'), 156.7 (C-2,2') ppm. IR (KBr): $\tilde{v} = 3074$ (w), 3055 (w), 3024 (w), 2960 (m), 2124 (m), 2115 (m), 1611 (s), 1594 (m), 1485 (m), 1416 (m), 1250 (m), 1230 (m), 1221 (m), 950 (m), 871 (m), 845 (s), 753 (m), 692 (m) cm⁻¹. MS (MALDI-TOF, dithranol): m/z = 745 [M]⁺, 1490 [2 M]⁺. C₃₆H₃₄N₂PtSi₂ (745.94): calcd. C 57.97, H 4.59, N 3.76; found C 57.93, H 4.62, N 3.58.

Bis(4-hexylphenylethynyl)[4,4'-bis(trimethylsilylethynyl)-2,2'-bipyridine]platinum(II) (6b): Compound 5 (0.08 g, 0.130 mmol) was dissolved in DCM (30 mL) and diisopropylamine (2 mL) under argon. CuI (3 mg, 0.014 mmol) and 1-ethynyl-4-hexylbenzene (0.073 g, 0.391 mmol) were added. The reaction mixture was stirred at room temp. overnight. The solvent was removed in vacuo, and the residue was purified by column chromatography with alumina and PE/ DCM (1:1). Product 6b (90 mg, 0.098 mmol, 75%) remained as a dark-brown solid. $R_{\rm f}$ = 0.78 (alumina, DCM/PE, 1:1). ¹H NMR (400 MHz, CD₂Cl₂): δ = 0.34 (s, 18 H, 6×CH₃), 0.89–0.93 (m, 6 H, H-12''), 1.31-1.41 (m, 12 H, H-9'', H-10'', H-11''), 1.60-1.67 (m, 4 H, H-8''), 2.62 (t, ${}^{3}J$ = 7.7 Hz, 4 H, H-7''), 7.12 (d, ${}^{3}J$ = 8.0 Hz, 4 H, H-5''), 7.38 (d, ${}^{3}J$ = 8.0 Hz, 4 H, H-4''), 7.55 (dd, ${}^{4}J$ = 1.5 Hz, ${}^{3}J$ = 5.8 Hz, 2 H, H-5,5'), 8.01 (d, ${}^{4}J$ = 1.4 Hz, 2 H, H-4,4'), 9.68 (d, ${}^{3}J$ = 5.8 Hz, 2 H, H-6,6') ppm. ${}^{13}C$ NMR (100 MHz, CD_2Cl_2 : $\delta = 0.0 \ (6 \times CH_3), 14.7 \ (C-12''), 23.5 \ (C-11''), 29.9 \ (C-12''), 29.9$ 10''), 32.3 (C-9''), 32.6 (C-8''), 36.6 (C-7''), 86.4 (C-2''), 101.4 $(C \equiv C-TMS)$, 103.0 (C-1''), 106.7 (C $\equiv C$ -bpy), 126.0 (C-5,5'), 125.9 (C-3''), 128.8 (C-5''), 130.3 (C-3,3'), 132.5 (C-4''), 134.7 (C-4,4'), 141.5 (C-6''), 151.8 (C-6,6'), 156.8 (C-2,2') ppm. IR (KBr): $\tilde{v} =$ 2958 (m), 2927 (s), 2855 (m), 2115 (m), 1635 (m), 1612 (s), 1504 (s), 1481 (w), 1416 (m), 1250 (s), 1229 (m), 845 (s) cm⁻¹. MS (MALDI-TOF, dithranol): $m/z = 914 [M]^+$, 1825 [2 M]⁺. C₄₈H₅₈N₂PtSi₂ (914.26): calcd. C 63.06, H 6.39, N 3.06; found C 63.08, H 6.50, N 3.04.

(4,4'-Diethynyl-2,2'-bipyridine)bis(phenylethynyl)platinum(II) (7a): Complex 6a (23 mg, 0.031 mmol) was dissolved in DCM (9 mL) and methanol (1 mL), and KF (4 mg, 0.068 mmol) was added. Stirring at room temp. was continued overnight. The solvent was removed in vacuo, and the residue was purified by column chromatography with alumina and PE/DCM (1:2) and 100%DCM. Product 7a (12 mg, 0.020 mmol, 65%) remained as a brown powder. $R_f = 0.51$ (alumina, DCM). ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 3.78$ (s, 2 H, 2×C=CH), 7.18–7.22 (m, 2 H, H-6''), 7.28–7.32 (m, 4 H, H-5''), 7.46–7.49 (m, 4 H, H-4''), 7.67 (dd, ${}^{4}J$ = 1.6 Hz, ${}^{3}J = 5.8$ Hz, 2 H, H-5,5), 8.12 (d, ${}^{4}J = 1.2$ Hz, 2 H, H-3,3'), 9.76 $(d, {}^{3}J = 5.8 \text{ Hz}, 2 \text{ H}, \text{H-6,6'}) \text{ ppm. } {}^{13}\text{C NMR} (100 \text{ MHz}, \text{CD}_2\text{Cl}_2):$ $\delta = 80.6 \ (2 \times C \equiv C$ -bpy), 87.5 (C-2''), 98.9 (2 × C $\equiv C$ -H), 103.2 (C-1"), 126.2 (C-3"), 126.6 (C-5,5"), 128.7 (C-5", C-6"), 131.0 (C-3,3'), 132.6 (C-4''), 134.2 (C-4,4'), 152.0 (C-6,6'), 156.7 (C-2,2') ppm. IR (KBr): $\tilde{v} = 3295$ (m), 3201 (m), 3055 (w), 2119 (s), 2111 (s), 1614 (m), 1593 (m), 1486 (m), 1412 (w), 839 (w), 754 (m), 693 (m) cm⁻¹. MS (MALDI-TOF, dithranol): $m/z = 600 [M - H]^+$, 1202 [2 M]⁺. C₃₀H₁₈N₂Pt (601.58): calcd. C 59.90, H 3.02, N 4.66; found C 59.49, H 3.42, N 4.43.

(4,4'-Diethynyl-2,2'-bipyridine)bis(4-hexylphenylethynyl)platinum-(II) (7b): Complex 6b (60 mg, 0.066 mmol) was dissolved in DCM (15 mL) and methanol (2 mL), and KF (11 mg, 0.197 mmol) was added. Stirring was continued overnight. The solvent was removed in vacuo, and the residue was purified by column chromatography with alumina and DCM/PE (2:1 and 3:1). After drying in vacuo, 7b (48.4 mg, 0.063 mmol, 95%) remained as a brown solid. $R_f = 0.31$ (alumina, DCM/PE, 4:1). ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.91$ (t, ³J = 6.7 Hz, 6 H, H-12''), 1.31–1.38 (m, 12 H, H-9'', H-10'', H-11''), 1.59–1.66 (m, 4 H, H-8''), 2.61 (t, ³J = 7.7 Hz, 4 H, H-7''), 3.76 (s, 2 H, C=C*H*), 7.12 (d, ${}^{3}J$ = 8.0 Hz, 4 H, H-5''), 7.38 (d, ${}^{3}J$ = 8.0 Hz, 4 H, H-4''), 7.63 (dd, ${}^{4}J$ = 1.1 Hz, 2 H, ${}^{3}J$ = 5.7 Hz, H-5,5'), 8.10 (d, ${}^{4}J$ = 1.0 Hz, 2 H, H-3,3'), 9.75 (d, ${}^{3}J$ = 5.8 Hz, 2 H, H-6,6') ppm. 13 C NMR (100 MHz, CD₂Cl₂): δ = 14.7 (C-12''), 23.5 (C-11''), 29.9 (C-10''), 32.3 (C-9''), 32.6 (C-8''), 36.6 (C-7''), 86.1 (C-2''), 87.4 (C=C-H), 80.7 (C=C-bpy), 103.2 (C-1''), 125.9 (C-3''), 126.3 (C-5,5'), 128.8 (C-5''), 130.8 (C-3,3'), 132.5 (C-4''), 134.0 (C-4,4'), 141.6 (C-6''), 151.9 (C-6,6'), 156.7 (C-2,2') ppm. IR (KBr): \tilde{v} = 2955 (m), 2925 (s), 2854 (m), 2115 (m), 1633 (m), 1611 (s), 1504 (s), 1478 (w), 1411 (m), 1229 (w), 843 (w) cm⁻¹. MS (MALDI-TOF, dithranol): m/z = 768 [M]⁺, 1538 [2 M]⁺. C₄₂H₄₂N₂Pt (769.90): calcd. C 65.52, H 5.50, N 3.64; found C 65.14, H 5.68, N 3.29.

[4,4'-Bis(1-benzyl-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine]bis(phenylethynyl)platinum(II) (8a): Complex 6a (60 mg, 0.080 mmol) was dissolved in DCM (24 mL) and methanol (6 mL), and KF (12 mg, 0.201 mmol) was added under argon. Cu(CH₃CN)₄PF₆ (9 mg, 0.024 mmol), DIPEA (0.05 mL, 0.32 mmol, 41 mg), elemental copper (2 mg, 0.024 mmol) and benzyl azide (27 mg, 0.201 mmol) were added. Stirring was continued at room temp. for 2 d. 25% ammonia (5 mL) in water (15 mL) and DCM (50 mL) were added. After stirring the solution vigorously for some minutes, the layers were separated and the aqueous layer was extracted with DCM (50 mL). The organic layer was washed with 0.1 M Na₂/EDTA solution and dried with Na₂SO₄. The solvent was removed in vacuo, and the residue was purified by column chromatography with silica and DCM/diethyl ether (5:1). The solid was dissolved in DCM and PE was added to precipitate the yellow powder, which was collected by filtration, washed with PE and dried in vacuo. Product 8a (57 mg, 0.065 mmol, 81%) was obtained as a yellow powder. $R_{\rm f} = 0.53$ (silica, DCM/diethyl ether, 10:1). ¹H NMR (500 MHz, [D₆]DMSO, 375 K): $\delta = 5.80$ (s, 4 H, H-benzyl), 7.19–7.22 (m, 2 H, H-6''), 7.31-7.34 (m, 4 H, H-5"), 7.41-7.49 (m, 14 H, H-Ph, H-4"), 8.33 $(dd, {}^{4}J = 1.7 Hz, {}^{3}J = 5.9 Hz, 2 H, H-5,5'), 9.05 (d, {}^{4}J = 1.4 Hz, 2$ H, H-3,3'), 9.06 (s, 2 H, H-5'''), 9.68 (d, ${}^{3}J$ = 5.9 Hz, 2 H, H-6,6') ppm. ¹³C NMR (125 MHz, [D₆]DMSO, 375 K): δ = 54.1 (Cbenzyl), 89.8 (C-2''), 101.6 (C-1''), 120.0 (C-3,3'), 123.7 (C-5'''), 125.6 (C-5,5'), 125.7 (C-3''), 128.3 (C-o-Ph), 128.4 (C-m-Ph), 128.6 (C-q-Ph), 128.8 (C-p-Ph) 129.3 (C-5", C-6"), 131.6 (C-4"), 135.8 (C-4,4'), 143.8 (C-4'''), 150.9 (C-6,6'), 157.1 (C-2,2') ppm. IR (KBr): $\tilde{v} = 3106$ (w), 3086 (w), 3049 (w), 3034 (w), 2925 (w), 2123 (m), 2111 (m), 1709 (w), 1626 (s), 1594 (m), 1569 (w), 1487 (m), 1456 (m), 1437 (m), 1359 (w), 1234 (m), 1215 (w), 1093 (w), 1047 (w), 1029 (w), 840 (w), 755 (m), 735 (m), 725 (m), 693 (m) cm⁻¹. MS (MALDI-TOF, dithranol): $m/z = 867 [M]^+$, 763 [M – PhAc]⁺. C44H32N8Pt (867.88): calcd. C 60.89, H 3.72, N 12.91; found C 60.65, H 3.74, N 12.88.

[4,4'-Bis(1-benzyl-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine]bis(hexylphenylethynyl)platinum(II) (8b): Complex 6b (64 mg, 0.070 mmol) was dissolved in DCM (24 mL) and methanol (6 mL), and KF (10 mg, 0.175 mmol) was added under argon. The solution was degassed, and Cu(CH₃CN)₄PF₆ (7 mg, 0.021 mmol), DIPEA (0.05 mL, 0.280 mmol, 36 mg), elemental copper (1 mg, 0.021 mmol) and benzyl azide (24 mg, 0.175 mmol) were added. The synthesis and purification were carried out as described above for 8a. Product 8b (61 mg, 0.059 mmol, 84%) was obtained as an orange powder. $R_{\rm f} = 0.20$ (silica, DCM/diethyl ether, 15:1). ¹H NMR (400 MHz, CD_2Cl_2): $\delta = 0.89-0.92$ (m, 6 H, H-12''), 1.28-1.39 (m, 12 H, H-9", H-10", H-11"), 1.59-1.66 (m, 4 H, H-8"), 2.59–2.63 (m, 4 H, H-7''), 5.36 (s, 4 H, H-benzyl), 7.09 (d, ${}^{3}J$ = 8.1 Hz, 4 H, H-5''), 7.24 (d, ${}^{3}J$ = 8.1 Hz, 4 H, H-4''), 7.27–7.28 (m, 4 H, H-o-Ph), 7.34–7.36 (m, 6 H, H-m, p-Ph), 7.77 (dd, ${}^{4}J$ = 1.5 Hz, ${}^{3}J$ = 5.9 Hz, 2 H, H-5,5'), 8.40 (s, 2 H, H-5'''), 8.53 (d, ${}^{4}J$

= 1.0 Hz, 2 H, H-3,3'), 9.36 (d, ${}^{3}J$ = 5.9 Hz, 2 H, H-6,6') ppm. ${}^{13}C$ NMR (100 MHz, CD₂Cl₂): δ = 14.7 (C-12''), 23.5 (C-11''), 29.9 (C-10''), 32.3 (C-9''), 32.6 (C-8''), 36.6 (C-7''), 55.1 (C-benzyl), 87.4 (C-2''), 102.8 (C-1''), 120.1 (C-3,3'), 123.7 (C-5'''), 124.9 (C-5,5'), 126.0 (C-3''), 129.0 (C-m-Ph), 129.1 (C-a,q-Ph), 129.6 (C-p-Ph), 129.9 (C-5''), 132.4 (C-4''), 135.3 (C-4,4'), 141.6 (C-6''), 144.5 (C-4'''), 151.4 (C-6,6'), 157.1 (C-2,2') ppm. IR (KBr): \tilde{v} = 2954 (w), 2926 (m), 2854 (m), 2113 (m), 1624 (s), 1503 (m), 1556 (m), 1437 (m), 1237 (m), 826 (m), 726 (m) cm⁻¹. MS (MALDI-TOF, dithranol): m/z = 1035 [M]⁺. C₅₆H₅₆N₈Pt (1036.20): calcd. C 64.91, H 5.45, N 10.81; found C 64.81, H 5.54, N 10.94.

Bis(phenylethynyl)[4,4'-bis(1-phenyl-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine|platinum(II) (8c): Complex 6a (60 mg, 0.080 mmol) was dissolved in DCM (24 mL) and methanol (6 mL), and KF (12 mg, 0.201 mmol) was added under argon. The solution was degassed, and Cu(CH₃CN)₄PF₆ (9 mg, 0.024 mmol), DIPEA (0.06 mL, 0.322 mmol, 42 mg), elemental copper (2 mg, 0.024 mmol) and phenyl azide (24 mg, 0.201 mmol) were added. The synthesis and purification were carried out as described above for 8a. Product 6a (55 mg, 0.066 mmol, 83%) was obtained as an orange powder. $R_{\rm f}$ = 0.19 (silica, DCM/diethyl ether, 10:1). ¹H NMR (400 MHz, CDCl₃): δ = 7.14–7.17 (m, 2 H, H-6^{''}), 7.22–7.25 (m, 4 H, H-5^{''}), 7.39 (d, ${}^{3}J = 7.3$ Hz, 4 H, H-4''), 7.52–7.58 (m, 6 H, H-*m*,*p*-Ph), 7.87–7.89 (m, 4 H, H-*o*-Ph), 8.05 (dd, ${}^{4}J$ = 1.7 Hz, ${}^{3}J$ = 6.0 Hz, 2 H, H-5,5'), 8.86 (s, 2 H, H-5'''), 8.96 (s, 2 H, H-3,3'), 9.70 (d, ³J = 5.7 Hz, 2 H, H-6,6') ppm. ¹H NMR (500 MHz, [D₆]DMSO, 375 K): δ = 7.20–7.23 (m, 2 H, H-6''), 7.31–7.34 (m, 4 H, H-5''), 7.43-7.45 (m, 4 H, H-4''), 7.61-7.64 (m, 2 H, H-p-Ph), 7.71-7.74 (m, 4 H, H-*m*-Ph), 8.00–8.02 (m, 4 H, H-*o*-Ph), 8.42 (dd, ${}^{4}J$ = 1.7 Hz, 2 H, ${}^{3}J$ = 5.8 Hz, H-5,5'), 9.17 (d, ${}^{4}J$ = 1.3 Hz, 2 H, H-3,3'), 9.69 (s, 2 H, H-5'''), 9.75 (d, ${}^{3}J$ = 5.8 Hz, 2 H, H-6,6') ppm. IR (KBr): $\tilde{v} = 3103$ (w), 3072 (m), 2957 (w), 2923 (w), 2111 (m), 1623 (s), 1596 (m), 1504 (m), 1486 (m), 1425 (m), 1245 (w), 1034 (m), 755 (m), 689 (m) cm⁻¹. MS (MALDI-TOF, dithranol): m/z =838 [M]⁺. C₄₂H₂₈N₈Pt (839.83): calcd. C 60.07, H 3.36, N 13.34; found C 60.07, H 3.40, N 13.07.

Bis(4-hexylphenylethynyl)[4,4'-bis(1-phenyl-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine]platinum(II) (8d): Complex 6b (67 mg, 0.073 mmol) was dissolved in DCM (24 mL) and methanol (6 mL), and KF (11 mg, 0.183 mmol) was added under argon. The solution was degassed, and Cu(CH₃CN)₄PF₆ (8 mg, 0.022 mmol), DIPEA (0.05 mL, 0.293 mmol, 38 mg), elemental copper (1 mg, 0.022 mmol) and phenyl azide (22 mg, 0.183 mmol) were added. The synthesis and purification were carried out as described above for 8a. Product 8d (54 mg, 0.053 mmol, 73%) was obtained as a yellow powder. $R_{\rm f} = 0.46$ (silica, DCM/diethyl ether, 25:1). ¹H NMR (400 MHz, CD_2Cl_2): $\delta = 0.89-0.91$ (m, 6 H, H-12''), 1.30-1.36 (m, 12 H, H-9", H-10", H-11"), 1.56-1.57 (m, 4 H, H-8"), 2.55–2.59 (m, 4 H, H-7''), 7.05 (d, ${}^{3}J$ = 8.1 Hz, 4 H, H-5''), 7.29 $(d, {}^{3}J = 8.0 \text{ Hz}, 4 \text{ H}, \text{H}-4''), 7.51-7.58 \text{ (m, 6 H, H-m,p-Ph)}, 7.88-$ 7.90 (m, 4 H, H-*o*-Ph), 8.06 (dd, ${}^{4}J$ = 1.8 Hz, 2 H, ${}^{3}J$ = 5.8 Hz, H-5,5'), 8.91 (s, 2 H, H-5'''), 8.97 (s, 2 H, H-3,3'), 9.73 (d, ${}^{3}J$ = 5.8 Hz, 2 H, H-6,6') ppm. IR (KBr): \tilde{v} = 2953 (m), 2926 (m), 2853 (m), 2120 (m), 2111 (m), 1624 (s), 1598 (m), 1504 (s), 1247 (m), 1034 (m), 824 (m), 759 (m) cm⁻¹. MS (MALDI-TOF, dithranol): $m/z = 1008 \text{ [M]}^+$, 2015 [2 M] $^+$. C₅₄H₅₂N₈Pt (1008.15): calcd. C 64.34, H 5.20, N 11.12; found C 64.47, H 5.32, N 10.98.

[4,4'-Bis{1-(4-hexylphenyl)-1*H*-1,2,3-triazol-4-yl}-2,2'-bipyridine]bis-(phenylethynyl)platinum(II) (8e): Complex 6a (0.122 g, 0.164 mmol) was dissolved in DCM (40 mL) and methanol (10 mL), and KF (24 mg, 0.410 mmol) was added under argon. The solution was degassed, and Cu(CH₃CN)₄PF₆ (18 mg, 0.049 mmol), DIPEA (0.1 mL, 0.491 mmol, 64 mg), elemental copper (3 mg, 0.049 mmol) and 4-hexylphenyl azide (83 mg, 0.401 mmol) were added. The synthesis and purification were carried out as described above for 8a. Product 8e (0.130 g, 0.129 mmol, 79%) remained as an orange powder. $R_{\rm f} = 0.57$ (silica, DCM/diethyl ether, 25:1). ¹H NMR (400 MHz, CD_2Cl_2): $\delta = 0.89-0.93$ (m, 6 H, H-15'''), 1.30-1.37 (m, 12 H, H-12''', H-13''', H-14'''), 1.60-1.66 (m, 4 H, H-11'''), 2.65 (t, ${}^{3}J = 7.7 \text{ Hz}$, 4 H, H-10'''), 7.04–7.13 (m, 6 H, H-5'', H-6''), 7.19–7.20 (m, 4 H, H-4''), 7.24 (d, ${}^{3}J$ = 8.4 Hz, 4 H, H-8'''), 7.71 (d, ${}^{3}J = 8.4 \text{ Hz}, 4 \text{ H}, \text{H-7''})$, 7.92 (d, ${}^{3}J = 5.8 \text{ Hz}, 2 \text{ H}, \text{H-5}, 5')$, 8.84 (s, 2 H, H-3,3'), 8.92 (s, 2 H, H-5'''), 9.40 (d, ${}^{3}J$ = 5.8 Hz, 2 H, H-6,6') ppm. ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 14.7$ (C-15'''), 23.5 (C-14'''), 29.7 (C-13'''), 32.0 (C-12'''), 32.5 (C-11'''), 36.2 (C-10'''), 88.4 (C-2''), 102.7 (C-1''), 120.5 (C-3,3'), 120.9 (C-8'''), 122.9 (C-5,5'), 123.3 (C-5'''), 126.3 (C-3''), 128.1 (C-6''), 128.5 (C-5''), 130.2 (C-7'''), 132.1 (C-4''), 135.0 (C-4,4'), 141.3 (C-6'''), 144.4 (C-4'''), 144.9 (C-9'''), 150.6 (C-6,6'), 156.6 (C-2,2') ppm. IR (KBr): $\tilde{v} = 3074$ (w), 3050 (w), 2954 (m), 2926 (s), 2854 (m), 2122 (m), 2111 (m), 1623 (s), 1593 (m), 1518 (s), 1485 (m), 1443 (m), 1246 (m), 1036 (m), 838 (m), 755 (m) cm⁻¹. HRMS (ESI): m/z

calcd. for $C_{54}H_{52}N_8Pt \ [M]^+$ 1008.4039; found 1008.4003.

(2,2'-Bipyridine)bis(phenylethynyl)platinum(II) (9):^[21] CODPt- $(C \equiv CPh)_2$ (0.05 g, 0.099 mmol) and 2,2'-bipyridine (0.016 g, 0.104 mmol) were dissolved in tetrahydrofuran (30 mL) and DCM (10 mL). The solution was degassed and subsequently heated under reflux for 3 d. The solvent was removed in vacuo, and the residue was purified by column chromatography with silica and DCM/diethyl ether (25:1). Product 9 (23 mg, 0.042 mmol, 42%) remained as a yellow solid. $R_f = 0.43$ (silica, DCM/diethyl ether, 25:1). ¹H NMR (400 MHz, CD_2Cl_2): $\delta = 7.18-7.12$ (m, 2 H, H-6''), 7.28-7.32 (m, 4 H, H-5''), 7.47-7.49 (m, 4 H, H-4''), 7.55-7.58 (m, 2 H, H-5,5'), 8.13–8.19 (m, 4 H, H-3,3', H-4,4'), 9.66 (d, ${}^{3}J$ = 4.3 Hz, 2 H, H-6,6') ppm. ¹H NMR (500 MHz, [D₆]DMSO, 375 K): δ = 7.18-7.12 (m, 2 H, H-6''), 7.29-7.32 (m, 4 H, H-5''), 7.38-7.40 (m, 4 H, H-4''), 7.86–7.89 (m, 2 H, H-5,5'), 8.37–8.40 (m, 2 H, H-4,4'), 8.58 (d, ${}^{3}J$ = 8.0 Hz, 2 H, H-3,3') 9.64 (d, ${}^{3}J$ = 4.6 Hz, 2 H, H-6,6') ppm. ¹³C NMR (100 MHz, CD₂Cl₂): δ = 88.0 (C-2''), 102.5 (C-1''), 123.9 (C-3,3'), 126.4 (C-3''), 128.2 (C-5,5'), 128.9 (C-5'', C-6''), 132.5 (C-4''), 139.8 (C-4,4'), 151.8 (C-6,6'), 157.0 (C-2,2') ppm. ¹³C NMR (125 MHz, [D₆]DMSO, 375 K): δ = 89.5 (C-2''), 101.9 (C-1''), 125.5 (C-3,3'), 126.1 (C-3''), 128.7 (C-5,5'), 128.8 (C-5", C-6"), 132.0 (C-4"), 140.3 (C-4,4"), 150.9 (C-6,6"), 156.8 (C-2,2') ppm. IR (KBr): $\tilde{v} = 3074$ (w), 3052 (w), 2122 (m), 2113 (s), 1605 (m), 1593 (m), 1485 (s), 1449 (m), 1160 (m), 1068 (m), 757 (s), 695 (m) cm⁻¹. MS (MALDI-TOF, dithranol): m/z = 553 [M]⁺, 1107 [2 M]⁺. C₂₆H₁₈N₂Pt (553.53): calcd. C 56.42, H 3.28, N 5.06; found C 56.33, H 3.28, N 4.92.

Supporting Information (see footnote on the first page of this article): Absorption, excitation and emission spectra of all complexes are provided in the Supporting Information.

Acknowledgments

We thank the Dutch Polymer Institute (DPI) for funding the project. This research formed part of the research programme of the DPI, within project 628.



a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151–154; b) R. C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S. R. Forrest, *Chem. Mater.* **1999**, *11*, 3709–3713; c) H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials*, 1st ed., Wiley-

FULL PAPER

VCH, Weinheim, Germany, **2007**; d) D. A. K. Vezzu, J. C. Deaton, J. S. Jones, L. Bartolotti, C. F. Harris, A. P. Marchetti, M. Kondakova, R. D. Pike, S. Huo, *Inorg. Chem.* **2010**, *49*, 5107–5119; e) G. Zhou, Q. Wang, X. Wang, C.-L. Ho, W.-Y. Wong, D. Ma, L. Wang, Z. Lin, *J. Mater. Chem.* **2010**, *20*, 7472–7484.

- [2] a) K. M.-C. Wong, W.-S. Tang, B. W.-K. Chu, N. Zhu, V. W.-W. Yam, Organometallics 2004, 23, 3459–3465; b) W.-S. Tang, X.-X. Lu, K. M.-C. Wong, V. W.-W. Yam, J. Mater. Chem. 2005, 15, 2714–2720; c) P. K. M. Siu, S.-W. Lai, W. Lu, N. Zhu, C.-M. Che, Eur. J. Inorg. Chem. 2003, 2749–2752; d) Y. Ji, R. Zhang, X.-B. Du, J.-L. Zuo, X.-Z. You, Dalton Trans. 2008, 2578–2582.
- [3] a) A. Scarpaci, C. Monnereau, N. Hergué, E. Blart, S. Legoupy, F. Odobel, A. Gorfo, J. Pérez-Moreno, K. Clays, I. Asselberghs, *Dalton Trans.* 2009, 4538–4546; b) P. Jarosz, K. Lotito, J. Schneider, D. Kumaresan, R. Schmehl, R. Eisenberg, *Inorg. Chem.* 2009, 48, 2420–2428; c) B. Ventura, A. Barbieri, A. Zanelli, F. Barigelletti, J. B. Seneclauze, S. Diring, R. Ziessel, *Inorg. Chem.* 2009, 48, 6409–6416; d) Z. Ji, Y. Li, T. M. Pritchett, N. S. Makarov, J. E. Haley, Z. Li, M. Drobizhev, A. Rebane, W. Sun, *Chem. Eur. J.* 2011, 17, 2479–2491.
- [4] a) F. Camerel, R. Ziessel, B. Donnio, C. Bourgogne, D. Guillon, M. Schmutz, C. Iacovita, J.-P. Bucher, Angew. Chem. 2007, 119, 2713; Angew. Chem. Int. Ed. 2007, 46, 2659–2662; b) C. Yu, K. H.-Y. Chan, K. M.-C. Wong, V. W.-W. Yam, Proc. Natl. Acad. Sci. USA 2006, 103, 19652–19657; c) M.-Y. Yuen, V. A. L. Roy, W. Lu, S. C. F. Kui, G. S. M. Tong, M.-H. So, S. S.-Y. Chui, M. Muccini, J. Q. Ning, S. J. Xu, C.-M. Che, Angew. Chem. 2008, 120, 10043; Angew. Chem. Int. Ed. 2008, 47, 9895–9900; d) C. A. Strassert, C.-H. Chien, M. D. Galvez Lopez, D. Kourkoulos, D. Hertel, K. Meerholz, L. De Cola, Angew. Chem. Int. Ed. 2011, 50, 946–950; e) K. M.-C. Wong, V. W.-W. Yam, Acc. Chem. Res. 2011, 44, 424–434.
- [5] a) M. Kato, Bull. Chem. Soc. Jpn. 2007, 80, 287–294; b) W. Lu,
 M. C. W. Chan, N. Zhu, C.-M. Che, Z. He, K.-Y. Wong, Chem. Eur. J. 2003, 9, 6155–6166; c) J. Ni, L.-Y. Zhang, H.-M. Wen,
 Z.-N. Chen, Chem. Commun. 2009, 3801–3803; d) J. Ni, X.
 Zhang, Y.-H. Wu, L.-Y. Zhang, Z.-N. Chen, Chem. Eur. J.
 2011, 17, 1171–1183.
- [6] a) L. Chassot, E. Müller, A. von Zelewsky, *Inorg. Chem.* 1984, 23, 4249–4253; b) D. Sandrini, M. Maestri, V. Balzani, L. Chassot, A. von Zelewsky, *J. Am. Chem. Soc.* 1987, 109, 7720–7724; c) J. Schneider, P. Du, X. Wang, W. W. Brennessel, R. Eisenberg, *Inorg. Chem.* 2009, 48, 1498–1506; d) M. K. Clark, S. Diring, P. Retailleau, D. R. McMillin, R. Ziessel, *Chem. Eur. J.* 2008, 14, 7168–7179; e) P. Shao, Y. Li, A. Azenkeng, M. R. Hoffmann, W. Sun, *Inorg. Chem.* 2009, 48, 2407–2419; f) J. Schneider, P. Du, P. Jarosz, T. Lazarides, X. Wang, W. W. Brennessel, R. Eisenberg, *Inorg. Chem.* 2009, 48, 4306–4317; g) P. H. Lanoe, J.-L. Fillaut, V. Guerchais, H. Le Bozec, J. A. G. Williams, *Eur. J. Inorg. Chem.* 2011, 1255–1259; h) A. F. Rausch, L. Murphy, J. A. G. Williams, H. Yersin, *Inorg. Chem.* 2009, 48, 11407–11414; i) A. F. Rausch, U. V. Monkowius, M. Zable, H. Yersin, *Inorg. Chem.* 2010, 49, 7818–7825.
- [7] a) I. Eryaici, C. N. Moorefield, G. R. Newkome, *Chem. Rev.* 2008, 108, 1834–1895; b) R. J. Mureinik, M. Bidani, *Inorg. Nucl. Chem. Lett.* 1977, 13, 625–629; c) R. Büchner, J. S. Field, R. J. Haines, C. T. Cunningham, D. R. McMillin, *Inorg. Chem.* 1997, 36, 3952–3956; d) V. W.-W. Yam, R. P.-L. Teng, K. M.-C. Wong, K.-K. Cheung, *Organometallics* 2001, 20, 4476–4482; e) Q.-Z. Yang, L.-Z. Wu, Z.-X. Wu, L.-P. Zhang, C.-H. Tung, *Inorg. Chem.* 2002, 41, 5653–5655; f) Z. Ji, A. Azenkeng, M. Hoffmann, W. Sun, *Dalton Trans.* 2009, 7725–7733.
- [8] a) G. T. Morgan, F. H. Burstall, J. Chem. Soc. 1934, 965–971;
 b) K. D. Hodges, J. V. Rund, Inorg. Chem. 1975, 14, 525–528;
 c) A. Vogler, H. Kunkely, J. Am. Chem. Soc. 1981, 103, 1559–1560;
 d) V. M. Miskowski, V. H. Houlding, Inorg. Chem. 1989, 28, 1529–1533;
 e) V. M. Miskowski, V. H. Houlding, C.-M. Che, Y. Wang, Inorg. Chem. 1993, 32, 2518–2524;
 f) C.-W.

Chan, L.-K. Cheng, C.-M. Che, *Coord. Chem. Rev.* **1994**, *132*, 87–97; g) S. L. James, M. Younus, P. R. Raithby, J. Lewis, *J. Organomet. Chem.* **1997**, *543*, 233–235; h) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2000**, *39*, 447–457; i) C. J. Adams, S. L. James, X. Liu, P. R. Raithby, L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.* **2000**, 63–67; j) C. E. Whittle, J. A. Weinstein, M. W. George, K. S. Schanze, *Inorg. Chem.* **2001**, *40*, 4053–4062; k) S.-C. Chan, M. C. W. Chan, Y. Wang, C.-M. Che, K.-K. Cheung, N. Zhu, *Chem. Eur. J.* **2001**, *7*, 4180–4190; l) J. Ni, X. Zhang, N. Qiu, Y.-H. Wu, L.-Y. Zhang, J. Zhang, Z.-N. Chen, *Inorg. Chem.* **2011**, *50*, 9090–9096.

- [9] a) F. Hua, S. Kinayyigit, J. R. Cable, F. N. Castellano, *Inorg. Chem.* 2005, 44, 471–473; b) F. N. Castellano, I. E. Pomestchenko, E. Shikhova, F. Hua, M. L. Muro, N. Rajapakse, *Coord. Chem. Rev.* 2006, 250, 1819–1828; c) F. Hua, S. Kinayyigit, J. R. Cable, F. N. Castellano, *Inorg. Chem.* 2006, 45, 4304–4306; d) F. Hua, S. Kinayyigit, A. A. Rachford, E. A. Shikhova, S. Goeb, J. R. Cable, C. J. Adams, K. Kirschbaum, A. A. Pinkerton, F. N. Castellano, *Inorg. Chem.* 2007, 46, 8771–8783.
- [10] a) A. Y.-Y. Tam, W. H. Lam, K. M.-C. Wong, N. Zhu, V. W.-W. Yam, *Chem. Eur. J.* 2008, *14*, 4562–4576; b) K. L. Garner, L. F. Parkes, J. D. Piper, J. A. G. Williams, *Inorg. Chem.* 2010, *49*, 476–487; c) H.-M. Wen, Y.-H. Wu, Y. Fan, L.-Y. Zhang, C.-N. Chen, Z.-N. Chen, *Inorg. Chem.* 2010, *49*, 2210–2221; d) C. J. Adams, N. Fey, Z. A. Harrison, I. V. Sazanovich, M. Towrie, J. A. Weinstein, *Inorg. Chem.* 2008, *47*, 8242–8257; e) C.-M. Che, C.-C. Kwok, S.-W. Lai, A. F. Rausch, W. J. Finkenzeller, N. Zhu, H. Yersin, *Chem. Eur. J.* 2010, *16*, 233–247; f) S.-Y. Chang, J. Kavitha, S.-W. Li, C.-S. Hsu, Y. Chi, Y.-S. Yeh, P.-T. Chou, G. H. Lee, A. J. Carty, Y.-T. Tao, C.-H. Chien, *Inorg. Chem.* 2006, *45*, 137–146; g) C.-T. Liao, H.-H. Chen, H.-F. Hsu, A. Poloek, H.-H. Yeh, Y. Chi, K.-W. Wang, C.-H. Lai, G.-H. Lee, C.-W. Shih, P.-T. Chou, *Chem. Eur. J.* 2011, *17*, 546–556.
- [11] a) J. A. G. Williams, *Top. Curr. Chem.* 2007, 281, 205–268; b) L. Murphy, J. A. G. Williams, *Top. Organomet. Chem.* 2010, 28, 75–111.
- [12] D. Ravindranathan, D. A. K. Vezzu, L. Bartolotti, P. D. Boyle, S. Huo, *Inorg. Chem.* 2010, 49, 8922–8928.
- [13] a) K. Feng, C. Zuniga, Y.-D. Zhang, D. Kim, S. Barlow, S. R. Marder, J. L. Brédas, M. Weck, *Macromolecules* 2009, 42, 6855–6864; b) F. Niedermair, M. Sandholzer, G. Kremser, C. Slugovc, *Organometallics* 2009, 28, 2888–2896; c) J.-Y. Cho, B. Domercq, S. Barlow, K. Y. Suponitsky, J. Li, T. V. Timofeeva, S. C. Jones, L. E. Hayden, A. Kimyonok, C. R. South, M. Weck, B. Kippelen, S. R. Marder, *Organometallics* 2007, 26, 4816–4829; d) P. T. Furuta, L. Deng, S. Garon, M. E. Thompson, J. M. J. Fréchet, *J. Am. Chem. Soc.* 2004, 126, 15388–15389; e) L. Deng, P. T. Furuta, S. Garon, J. Li, D. Kavulak, M. E. Thompson, J. M. J. Fréchet, *Chem. Mater.* 2006, 18, 386–395; f) F. Galbrecht, X. H. Yang, B. S. Nehls, D. Neher, T. Farrell, U. Schwerf, *Chem. Commun.* 2005, 2378–2380.
- [14] H. C. Kolb, M. G. Finn, K. B. Sharpless, Angew. Chem. 2001, 113, 2056; Angew. Chem. Int. Ed. 2001, 40, 2004–2021.
- [15] a) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, Angew. Chem. 2002, 114, 2708; Angew. Chem. Int. Ed. 2002, 41, 2596–2599; b) C. W. Tornoe, C. Christensen, M. Meldal, J. Org. Chem. 2002, 67, 3057–3064; c) V. D. Bock, H. Hiemstra, J. H. van Maarseveen, Eur. J. Org. Chem. 2006, 51–68; d) W. H. Binder, R. Sachsenhofer, Macromol. Rapid Commun. 2007, 28, 15–54; e) J.-F. Lutz, Angew. Chem. 2007, 119, 1036; Angew. Chem. Int. Ed. 2007, 46, 1018–1025.
- [16] P. F. H. Schwab, F. Fleischer, J. Michl, J. Org. Chem. 2002, 67, 443–449.
- [17] a) D. Wenkert, R. B. Woodward, J. Org. Chem. 1983, 48, 283–289; b) D. Zhang, E. J. Dufek, E. L. Clennan, J. Org. Chem. 2006, 71, 315–319; c) G. Maerker, F. H. Case, J. Am. Chem. Soc. 1958, 80, 2745–2748.
- [18] R. Romeo, L. M. Scolaro, Inorg. Synth. 1998, 32, 153-158.



- [19] H.-B. Xu, L.-Y. Zhang, Z.-L. Xie, E. Ma, Z.-N. Chen, Chem. Commun. 2007, 2744–2746.
- [20] K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi, N. Hagihara, J. Organomet. Chem. 1978, 145, 101–108.
- [21] H. Lang, A. del Villar, G. Rheinwald, J. Organomet. Chem. 1999, 587, 284–289.
- [22] J. Andersen, U. Madsen, F. Björkling, X. Liang, Synlett 2005, 2209–2213.
- [23] S. G. Alvarez, M. T. Alvarez, Synthesis 1997, 413-414.
- [24] a) I. Stengel, A. Mishra, N. Pootrakulchote, S.-J. Moon, S. M. Zakeeruddin, M. Grätzel, P. Bäuerle, *J. Mater. Chem.* 2011, 21, 3726–3734; b) S. Paek, C. Baik, M.-s. Kang, H. Kang, J. Ko, *J. Organomet. Chem.* 2010, 695, 821–826.
- [25] a) A. Wild, C. Friebe, A. Winter, M. D. Hager, U.-W. Grummt, U. S. Schubert, *Eur. J. Org. Chem.* 2010, 1859–1868; b) R. Westlund, E. Glimsdal, M. Lindgren, R. Vestberg, C. Hawker, C. Lopes, E. Malmström, *J. Mater. Chem.* 2008, *18*, 166–175; c) D. J. V. C. van Steenis, O. R. P. David, G. P. F. van Strijdonck, J. H. van Maarseveen, J. N. H. Reek, *Chem. Commun.* 2005, 4333–4335; d) P. D. Jarowski, Y.-L. Wu, B. Schweizer, F. Diederich, *Org. Lett.* 2008, *10*, 3347–3350.
- [26] a) H. Kunkely, A. Vogler, J. Am. Chem. Soc. 1990, 112, 5625–5627; b) K.-T. Wan, C.-M. Che, K.-C. Cho, J. Chem. Soc., Dalton Trans. 1991, 1077–1080; c) J.A. Bailey, M.G. Hill,

R. E. Marsh, V. M. Miskowski, W. P. Schaefer, H. B. Gray, *Inorg. Chem.* **1995**, *34*, 4591–4599; d) S. Delahaye, C. Loosli, S.-X. Liu, S. Decurtins, G. Labat, A. Neels, A. Loosli, T. R. Ward, A. Hauser, *Adv. Funct. Mater.* **2006**, *16*, 286–295.

- [27] G. L. Fuhrmann, Dissertation, **2006**, University of Ulm, Germany.
- [28] P. Zacharias, M. C. Gather, M. Rojahn, O. Nuyken, K. Meerholz, Angew. Chem. 2007, 119, 4467; Angew. Chem. Int. Ed. 2007, 46, 4388–4392.
- [29] T. Dingemans, D. J. Photinos, E. T. Samulski, A. F. Terzis, C. Wutz, J. Chem. Phys. 2003, 118, 7046–7061.
- [30] R. J. Cross, M. F. Davidson, J. Chem. Soc., Dalton Trans. 1986, 1987–1992.
- [31] J. X. McDermott, J. F. White, G. M. Whitesides, J. Am. Chem. Soc. 1976, 98, 6521–6528.
- [32] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed., Elsevier Science, New York, 2003.
- [33] a) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179; b) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.

Received: January 20, 2012 Published Online: March 1, 2012