Electrophosphorescent Heterobimetallic Oligometallaynes and Their Applications in Solution-Processed Organic Light-Emitting Devices

Guijiang Zhou,^{*[a]} Yue He,^[a] Bing Yao,^[b] Jingshuang Dang,^[a] Wai-Yeung Wong,^{*[c]} Zhiyuan Xie,^{*[b]} Xiang Zhao,^{*[a]} and Lixiang Wang^[b]

Abstract: By combining the iridium-(III) ppy-type complex (Hppy=2-phenylpyridine) with a square-planar platinum(II) unit, some novel phosphorescent oligometallaynes bearing dual metal centers (viz. Ir^{III} and Pt^{II}) were developed by combining trans-[Pt-(PBu₃)₂Cl₂] with metalloligands of iridium possessing bifunctional pendant acetylene groups. Photophysical and computational studies indicated that the phosphorescent excited states arising from these oligometallaynes can be ascribed to the triplet emissive Ir^{III} ppy-type chromophore, owing to the obvious trait (such as the longer phosphorescent lifetime at 77 K) also conferred by the Pt^{II} center. So, the two different metal centers show a synergistic effect in governing the photophysical behavior of these heterometallic oligometallaynes. The inherent nature of these amorphous materials renders the fabrication of simple solution-processed doped phosphorescent organic light-emitting diodes (PHOLEDs) feasible by effectively blocking the close-

Keywords: alkynes • bimetallic • organic light-emitting diodes • phosphorescence • polymetallaynes

[a] Prof. G. Zhou, Y. He, J. Dang, Prof. X. Zhao MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter and Department of Chemistry Faculty of Science Xi'an Jiao Tong University Xi'an 710049 (P.R. China) Fax: (+86)29-82663914 E-mail: xzhao@mail.xjtu.edu.cn zhougj@mail.xjtu.edu.cn [b] B. Yao, Prof. Z. Xie, Prof. L. Wang State Key Laboratory of Polymer Physics and Chemistry Changchun Institute of Applied Chemistry Chinese Academy of Sciences Changchun 130022 (PR. China) Fax: (+86)431-5684937 E-mail: xiezy_n@ciac.jl.cn

 [c] Prof. W.-Y. Wong
 Institute of Molecular Functional Materials and Department of Chemistry and Centre for Advanced Luminescence Materials Hong Kong Baptist University
 Waterloo Road, Kowloon Tong, Hong Kong (P.R. China)
 Fax: (+852)3411-7348
 E-mail: rwywong@hkbu.edu.hk

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201000341.

ly, such a synergistic effect is also important in affording decent device performance for the solution-processed PHOLEDs. A maximum brightness of 3356 cdm^{-2} (or 2708 cdm^{-2}), external quantum efficiency of 0.50% (or 0.67%), luminance efficiency of $1.59 \text{ cd } \text{A}^{-1}$ (or $1.55 \text{ cd } \text{A}^{-1}$), and power efficiency of $0.60 \, Lm \, W^{-1}$ (or 0.55 Lm W^{-1}) for the yellow (or orange) phosphorescent PHOLEDs can be obtained. These results show the great potential of these bimetallic emitters for organic light-emitting diodes.

packing of the host molecules. Salient-

Introduction

Since the successful synthesis of Zeise's salt $K[PtCl_3(C_2H_4)]$ in 1827, organometallic complexes have always been an active research field in the scientific community for not only their unique structures and bonding features but also their intrinsic properties, showing potential applications associated with new material synthesis,^[1] ion sensing,^[2] and utilization of new energy sources,^[3] and so forth. Owing to the inherent character of the metal center, transition-metal complexes show a tendency to chelate with certain chemical groups in molecules which will be activated for further chemical reaction with other reagents.^[4] Furthermore, the configuration of ligands in transition-metal complexes usually exert a great effect on the yield of the reaction and the structure or even the geometry of the final product.^[5] So, transition-metal complexes are very often effective catalysts for many organic transformations to bring about a diversity of molecules with special properties for new materials research. The photophysical behavior of some metalated complexes is sensitive to guest ions, such as CN⁻, F⁻, and so forth, in solution, hence, they can also play the role as ion

Chem. Asian J. 2010, 5, 2405-2414

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

View this journal online at wileyonlinelibrary.com

2405

sensors, which is an important topic for environment protection. Besides, the Pt^{II} polymetallaynes and Ru^{II} bipyridinetype molecules are able to function as high-performance optoelectronic materials for bulk-heterojunction polymer and dye-sensitized solar cells^[3,6] and highly transparent optical power limiters.^[7]

Owing to the large spin-orbit coupling constant of heavy transition-metal atoms, significant triplet (or phosphorescent) state characters are associated with many transitionmetal complexes, especially for the third-row transitionmetal (Re^I, Os^{II}, Ir^{III}, and Pt^{II})^[8-11] complexes. Successfully harnessing both of the singlet and triplet excited states in triplet emitters has brought revolutionary progress to the field of organic light-emitting diodes (OLEDs). Traditional singlet/fluorescent emitters will favor a 3:1 ratio of the nonemissive triplet states over singlet states according to the quantum spin statistics prediction for the free charge-carriers, which severely limits device efficiency.^[12] Among all the known triplet emitters/phosphors, the unique photophysical features associated with Ir^{III} and Pt^{II} ppy-type (Hppy=2phenylpyridine) complexes, such as tunable emission color, high phosphorescent quantum yield $(\Phi_{\rm p})$, relatively short lifetime (τ_p) , and so forth, would definitely place them in a favorable position to meet the

targets in both full-color flatpanel displays and low-cost lighting sources.

While there are numerous potential uses of transitionmetal complexes nowadays, we are confident that new applications or improved performances would emerge as other new materials continue to be developed. Recently, the burgeoning field of polymetallaynes (especially polyplatinynes) is gaining momentum through continued breakthroughs in materials design and device engineering.^[6b-f,7] The innovative design of these functional metal polyynes has been demonstrated to be useful in energy-producing (solar cells) and energy-saving (OLEDs) applications. Though still in its infancy, the idea of incorporating two transition metals in a single metallopolyyne chain also has significant appeal and there are a few reports on using Au^I, Fe^{II}, Hg^{II}, Re^I, Ru^{II}, Pd^{II}, Pt^{II}, and so forth, in synthesizing bimetallic materials.^[7a, b, 13] metallavne While it is well-known that cyclometalated Ir^{III} complexes are promising light-emitting molecules in realizing phosphorescent small-molecule and polymer OLEDs, to our knowledge, linking these Ir^{III} moieties with polyplatinynes in some bimetallic materials should bring about the best of both worlds. In view of this, we present here the first examples of novel phosphorescent heteronuclear oligometallaynes consisting of dual metal centers (namely, Ir^{III} and Pt^{II}) in the main chain, and their photophysical behavior and potential light-emitting application will be described.

Results and Discussion

Synthetic Strategies and Chemical Characterization

Chemical structures and the detailed synthetic protocols of the new $Ir(C^{N})_2(acac)$ -based metalloligands **L1** and **L2** are shown in Scheme 1 (Hacac=acetylacetone, C^N=anionic cyclometalating ligand; also see Supporting Information). With the selective Stille coupling reaction,^[14a] the bromosubstituted ppy-type chelates were synthesized successfully. In order to avoid the side reactions under the reaction conditions for the trimethylsilylethynyl group, compounds **1** and **2** were prepared first. They then underwent a Sonogashira-



Scheme 1. Synthesis of the Ir^{III} metalloligands.

2406 www.chemasianj.org

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

type coupling reaction^[14b,c] to produce the ligand precursors **3** and **4**, respectively. After deprotection with a base under very mild conditions, **L1** and **L2** were obtained as orange solids in high yields of ~85% (see Supporting Information).

For the synthesis of the dual transition-metal-coordinated polyynes, each of the corresponding metalloligands reacts with *trans*-[Pt(PBu₃)₂Cl₂] in a 1:1 feed mole ratio through a dehydrohalogenation protocol under a CuI/Et₃N catalytic system (Scheme 2).^[15] The oligometallaynes **P1** and **P2** can be obtained as orange solids in good yields after precipitation from methanol.



Scheme 2. Synthesis of the bimetallic polymetallaynes of Ir^{III} and Pt^{II}.

The chemical structures of the metalloligands L1 and L2 have been characterized thoroughly by elemental analysis, NMR (¹H and ¹³C), and mass spectra (see Supporting Information). The characteristic signal for the terminal $C \equiv CH$ at approximately 3.00 ppm in each of the ¹H NMR spectra of L1 and L2 indicates that the functional group necessary for the dehydrohalogenative reaction remains intact. The structures of **P1** and **P2** were also characterized by NMR (¹H, ¹³C, and ³¹P) and GPC. The broad proton signals in their ¹H NMR spectra reveal their polyyne character. However, the GPC results show that the M_n for **P1** and **P2** is approximately 1.3×10^4 gmol⁻¹ and 1.1×10^4 gmol⁻¹, respectively. The relatively low M_n values with reference to the molecular weight of the metalloligand comonomer indicate that **P1** and **P2** are better described as oligomers, which can be revealed from the weak FT-IR absorption band at around 390 cm⁻¹ (Figure S1 in the Supporting Information) corresponding to the unreacted terminal Pt–Cl bond. The reso-

nance signal at about 4.00 ppm in the ³¹P-{¹H} NMR of the bimetallic polyynes indicates that the Pt(PBu₃)₂ moieties adopt a *trans* configuration in the oligomeric chain.

Thermal and Photophysical Properties

The thermal properties of the oligometallaynes with dual transition-metal centers were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere (Table 1). The TGA data reveal that all the metal complexes have excellent thermal stability and their 5% weight-reduction temperatures ($\Delta T_{5\%}$) exceed 320°C. Analysis of the DSC

traces for the polyynes showed no crystallization peaks but only glass-transition temperatures (T_g) , which can be attributed to the branched and tortuous configuration of the Ir- $(C^N)_2(acac)$ -centered moieties in the backbone of the oligometallaynes. There is a notable rise in the T_g from metalloligand to the corresponding oligometallaynes, indicating that the oligomerization process tends to hinder the

There is a notophysical and mornial and for the new engenerality is and then corresponding figure precautors.								
Compound	Absorption $\lambda_{abs} [nm]^{[a]}$ 293 K	Emission λ _{em} [nm] 293 K/77 K	$\pmb{\varPhi}_{\mathrm{p}}\left[\% ight]^{[\mathrm{b}]}$	τ _p [μs] ^[c] 293 K/77 K	τ _r [μs] ^[d] 293 K	$\Delta T_{5\%}/T_{\rm g} [{}^{\rm o}{ m C}]^{[{ m e}]}$		
P1	229, 260, 287, 379, 400, 446, 465, 487	549, 588/552, 599	12.3	0.11/10.82	14.83	320/140		
P2	229, 251, 283, 383, 400, 474, 502	577, 625/577, 631	4.8	0.51/12.12	6.26	334/172		
L1	227 (31330), 282 (63240), 304 (48055), 350 (8850), 377 (5880), 430 (4390), 464 (3195), 480 (2640)	538, 571/538, 581	23.5	0.21/4.99	5.43	330/110		
L2	229 (43225), 294 (39410), 341 (61180), 355 (55690), 400 (17220), 472 (5470), 489 (4760)	567, 608/567, 611	9.2	0.66/7.77	13.47	346/120		

Table 1. Photophysical and thermal data for the new oligometallaynes and their corresponding ligand precursors.

[a] Measured in CH₂Cl₂ at a concentration of 10^{-5} M and ε values are shown in parentheses. [b] In CH₂Cl₂ relative to *fac*-[Ir(ppy)₃] (Φ_p =0.40), λ_{ex} = 400 nm. [c] Measured in freeze-pump-thaw degassed CH₂Cl₂ solutions at a sample concentration of ca. 10^{-5} M and the excitation wavelength was set at 355 nm. [d] The triplet radiative lifetimes were deduced from $\tau_r = \tau_P / \Phi_P$ [e] $\Delta T_{5\%}$ is the 5% weight-reduction temperature and T_g is the glass transition temperature.

Chem. Asian J. 2010, 5, 2405-2414

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemasianj.org

mobility and flexibility of the chelating ligands and hence, a higher $T_{\rm g}$ was observed for the Ir/Pt-based oligometallaynes (140 °C for **P1** and 170 °C for **P2**) which are desirable for subsequent device study (vide infra).

Both P1 and P2 exhibit two major absorption bands in their UV/Vis spectra (Figure 1 a). The intense UV bands



Figure 1. a) Absorption and b) PL spectra of **P1** and **P2** and their metalloligand precursors in CH_2Cl_2 at 293 K.

near 400 nm are attributed to the spin-allowed ${}^{1}\pi-\pi^{*}$ transitions. The weaker, low-energy features result from both ${}^{1}MLCT$ and ${}^{3}MLCT$ (metal-to-ligand charge transfer) excitations. The strong spin-orbit coupling is confirmed by the similar oscillator strengths for the two MLCT bands (Table 1).^[11g] Compared with the absorption data of L1 and L2, the polyynes P1 and P2 show almost similar MLCT energy states to L1 and L2 while their spin-allowed ${}^{1}\pi-\pi^{*}$ transitions are shifted to a longer wavelength. Since the absorption behavior for the ground state has a close relationship with the characteristics of the molecular orbitals (especially for the HOMOs), we carried out time-dependent density functional theory (TD-DFT) computations for the compounds to elucidate their electronic properties.

Without loss of generality, the theoretical computations for **P1** and **P2** were made based on their repeat units to save the computation times. Such repeating units essentially serve as model compounds for the photophysical behavior of the polymeric molecules.^[7a,b] From the HOMO/HOMO-1 patterns for the repeat unit of P1 and P2 (Figure 2c and 2d and Table 2), the d_{π} orbitals of their Pt^{II} centers make clear contributions (12.5% for **P1** and 17.6% for **P2**, respectively) and the atomic contributions for a π system are distributed over the two main ligands bonded with the central trans-Pt- $(PBu_3)_2$ moiety, which would extend the conjugation length of Ir^{III}-based chromophore to afford lower-energy spin-allowed ${}^{1}\pi-\pi^{*}$ transitions.^[16] Such a marked difference for the ${}^{1}\pi$ - π^{*} transitions in metalloligands and oligometallaynes is consistent with the data in Figure 1a. From the distribution pattern of the frontier orbitals for L1 and L2 and the repeat units of P1 and P2, the MLCT transitions for both metalloligands and Pt/Ir polyynes involve similar electronic characters consisting of the d_{π} orbitals of the Ir^{III} center to the π orbitals of the pyridyl ring in the ligands, despite the fact that some contribution from the d_{π} orbitals of Pt^{II} moieties cannot be totally excluded. So, the absorption energies for the MLCT bands are similar for both the polyynes and their ligand precursors (Figure 1a).

Upon light irradiation at 400 nm, P1 and P2 both produce intense yellow/orange phosphorescence. Their emission spectra with obvious vibronic progressions indicate that the phosphorescent emissions of P1 and P2 mainly originate from the ligand-centered (LC) ${}^{3}\pi-\pi^{*}$ states, probably together with a small contribution from ³MLCT transitions (Figure 1b and Table 1). The structureless low-energy features may be caused by the vibronic coupling interactions (Figure 1b). In order to account for their photoluminescence (PL) behavior, we have examined their electronic structures which have a close relationship with the photophysical behavior. Our TD-DFT calculations show that the lowest-energy transitions correspond to the HOMO \rightarrow LUMO transitions with non-zero oscillator strengths and only the HOMO-LUMO transition is important for the first excited state (Table 2). From Table 2, it is shown that the MO compositions in S_1 are similar to those in T_1 in our systems. So, the HOMO-LUMO transition also contains the character for the T_1 states in the bimetallic polyynes and their metalloligands, which are the origin of the phosphorescence. Therefore, we focus our attention on the HOMO-LUMO analyses in the following discussion for their phosphorescent behavior. Similar to their absorption behavior, the *trans*-Pt(PBu₃)₂ moiety can extend the conjugation length along the main chain in P1 and P2, as can be revealed from their HOMO/HOMO-1 patterns and also those found in other reported Pt^{II}-arylacetylides.^[7a-c] Accordingly, the conjugation length of the ppy-type ligands chelated with an IrIII center is increased after copolymerization, which corroborates well with the observed red-shift of the ${}^{1}\pi$ - π * transitions in the metallopolyynes relative to their metalloligands (Figure 1a). Hence, the enhanced conjugation effect will lead to bathochromic behavior for the emission maxima of P1 and P2 (Figure 1b and Table 1). Furthermore, the photophysical investigation of Ir^{III} ppy-type complexes suggests that the triplet emission would typically exhibit more LC character with increasing conjugation length of the ligands,^[11h] which is reflected from the notably more struca)

AN ASIAN JOURNAL

peating unit of P1 and P2 in Figure 2, the lowest-energy excited state is largely dominated by the LC characteristics.

It is not expected that the lifetime for P1 and P2 is shorter at 293 K but longer at 77 K than that of their corresponding precursors L1 and L2. It is anticipated that the lifetime of the polymetallayne might be shortened at any temperature compared with that of the free ligand if they possess similar emissive triplet excited states, since copolymerization would link up the free monomers together which might cause a stronger quenching effect accordingly. Compared with those of L1 and L2, the much longer lifetimes for P1 and P2 at 77 K certainly need more careful attention here. It appears that the emissive triplet excited states probably exhibit different characters for the oligometallaynes and their metalloligands. From the HOMO electron distribution of the repeating units of P1 and **P2** (Figure 2 and Table 2), the contribution from the d_{π} orbitals of the Pt^{II} center (12.5% for P1 and 17.6% for P2) indicates that the $Pt^{\rm II}$ center can induce strong spin-orbit coupling.^[17] With reference to many Pt^{II}-centered bis(aryleneethynylene)s in the literature, the spin-orbit coupling effect would facilitate the triplet emission.^[7a-c] So, the emissive triplet excited states in P1 and P2 necessarily contain some phosphorescent character owing to the Pt^{II}-bis(aryleneethynylene) chromophore which is prone to be very temperature sensitive and possess much longer lifetimes compared with those induced by the Ir^{III} center in their



Figure 2. Contour plots of the highest occupied (HOMO-1 and HOMO) and lowest unoccupied (LUMO) molecular orbitals for a) L1, b) L2, c) repeating unit of P1 and d) repeating unit of P2.

tured line shape of the emission spectra on going from the metalloligands to the mixed-metal polyvnes, indicating that more LC ${}^{3}\pi-\pi^{*}$ excited states are involved in **P1** and **P2** (Figure 1b). By looking at the LUMO pattern of each re-

triplet emissive states for P1 and P2 at 77 K should consist of a significant contribution coming from the long-lived triplets of Pt^{II}-bis(aryleneethynylene) besides those from the Ir^{III}-centered moiety, which is not the case for L1 and L2. Hence, P1 and P2 show much

Ir ppy-type complexes. The

Table 2.	Percentage	contribution of	of the metal	d orbitals to	o HOMO	and LUMO	together wi	ith the	TD-DFT	calculation res	ults.
----------	------------	-----------------	--------------	---------------	--------	----------	-------------	---------	--------	-----------------	-------

compound	contribution of metal d	contribution of metal d	largest coefficient in the CI expansion of the T_1 state ^[a]	largest coefficient in the CI expansion of the S_1 state ^[a]	oscillator strength (f) of the $S_0 \rightarrow S_1$ transition
	orbitals to HOMO	orbitals to LUMO	$(S_0 \rightarrow I_1 \text{ excitation energy})$	$(\mathbf{S}_0 \rightarrow \mathbf{S}_1 \text{ excitation energy})$	
P1	12.54 % (Pt)	0.0021 % (Pt)	$H \rightarrow L: 0.11 \ (529 \ nm)$	$H \rightarrow L: 0.20 \ (484 \ nm)$	0.014
	1.23% (Ir1)	3.95% (Ir1)			
	13.37 % (Ir2)	0.00014% (Ir2)			
P2	17.59% (Pt)	0.0038% (Pt)	H→L: -0.13 (548 nm)	H→L: -0.31 (490 nm)	0.029
	1.84% (Ir1)	2.93% (Ir1)			
	4.26% (Ir2)	0.00037% (Ir2)			
L1	43.20% (Ir)	2.48% (Ir)	H→L: 0.61 (521 nm)	H→L: 0.67 (466 nm)	0.038
L2	50.13% (Ir)	3.34 % (Ir)	H→L: 0.65 (541 nm)	H→L: 0.68 (482 nm)	0.050

[a] H→L represents the HOMO to LUMO transition. CI stands for configuration interaction.

longer lifetimes at 77 K. At 293 K, the long-lived character for the triplet emissive states of **P1** and **P2** would become insignificant. As a result, the lifetime of the oligometallaynes is very similar to that of their corresponding metalloligands (Table 1).

Electrophosphorescent Characterization

The photophysical investigation described in the previous section shows that the new bimetallic oligometallaynes P1 and **P2** (**P1**: HOMO = -5.44 eV, LUMO = -3.00 eV, $E_{g} =$ 2.44 eV: **P2**: -5.46 eV,-3.07 eV, 2.39 eV) should be good phosphorescent materials. Moreover, their oligomeric nature would simplify electrophosphorescent OLED characterization by the solution processing techniques, so doped phosphorescent organic light-



Figure 3. The general configuration for the electrophosphorescent OLEDs and the molecular structures of the relevant compounds used in these devices.

emitting diodes (PHOLEDs) have been prepared. Figure 3 depicts the general structures of the PHOLEDs and the molecular structures of the compounds employed. 4,4'-N,N'-Dicarbazolebiphenyl (CBP) was used as the carrier recombination host for our metallophosphors owing to its ambipolar charge carrier-transporting properties and suitable triplet energy level. The composite polymer solution of PE-DOT:PSS (poly(3,4-ethylene-dioxythiophene)-poly(styrene sulfonate)) was first spin-coated on the ITO surface to serve as the hole-injection (HI) layer. Then, the emitting layer of polymetallayne dopant and CBP host was deposited by simple spin-coating method. Owing to the highly amorphous character of the emitter, the inclination for crystallization of CBP was hindered greatly and a good-quality emission layer was obtained. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthro-

line (BCP) was adopted as a hole-blocker, tris(8-hydroxyquinolinato)aluminum (Alq₃) as an electron-transporter, and LiF as an electron-injection material. All of the devices consist of the multilayer configuration ITO/PEDOT:PSS (40 nm)/x%dopant:CBP (50 nm)/BCP $(15 \text{ nm})/\text{Alq}_3$ (40 nm)/LiF:Al (1:100 nm). To optimize the device efficiency, concentration dependence experiments were carried out in the range of 5 to 20 wt %. When a proper voltage was applied to the devices, intense electrophosphorescence harnessed by the strong heavy-atom effect of Ir and $\mbox{Pt}^{[11i,j]}$ was observed (Figure 4 and Figure S2 in the Supporting Information). Devices A1-A3 with P1 as the emitter give yellow electrophosphorescence with an emission maximum at 552 nm while devices **B1–B3** made from **P2** exhibit orange electrophosphorescence with an emission maximum at



Figure 4. The EL spectra for the best devices (devices A2 and B2 at 10 wt% doping level) at 8 V.

580 nm. The close resemblance of the EL spectra with the corresponding PL spectra in each case indicates that the EL originates from the triplet states of the phosphorescent polymetallayne (Figure 4). No emission from CBP was observed from the EL spectra of devices A1-A3 and B1-B3, which indicates the effective energy transfer from CBP host to phosphorescent dopant (Figure S2 in the Supporting Information). However, the EL spectra for the devices with lower doping levels (1 wt% and 2 wt%) exhibit an obvious emission band from CBP (ca. 400 nm) and a broad emission peak (ca. 470 nm) from the exciplex of CBP as indicated by its structureless spectra, showing that a low amount of dopant cannot harness all the energy from the host and tend to block the packing arrangement among the host molecules (Figure S3 in the Supporting Information). Accordingly, devices with higher doping levels were made. When the doping level was increased to 5 wt%, the emission bands arising from CBP and its exci-

plex completely vanished (Figure S3 in the Supporting Information). So, the phosphorescent oligometallaynes can consume the energy from the host properly and provide a highly amorphous doped emission layer by virtue of the oligomeric character of the phosphorescent emitters, which is necessary for high-performance devices. Encouragingly, no obvious emission bands from the excimer formed by the packing of the emitting centers were detected even at the doping level as high as 20 wt % (Figure S2 in the Supporting Information). Hence, the advantage of the novel structures in P1 and P2 to block close-packing among

the emitting sites can be shown to result in a better emission color purity.

The luminance-voltage-current density (L-V-J) characteristics for the devices are shown in Figure 5 and Figure S4 in the Supporting Information. The key performance parame-



Figure 5. The L-V-J curves for devices A2 and B2.

ters for all the devices are summarized in Table 3 and it can be seen clearly that devices **A2** and **B2** with a doping level of 10 wt % give the best performance. They turned on at 5.9 and 5.2 V, respectively. Device **B2** produced the maximum luminance of about 2708 cdm⁻² at 15.4 V. The relatively high driving voltages with respect to the typical vacuumevaporated devices may arise from the thicker emissive layer of CBP:Ir dopant used and the large hole barrier at the PEDOT:PSS/CBP interface (HOMOs of CBP ~ -6.2 eV versus PEDOT ~ -5.0 eV). Device **A2** can even emit brighter light at the luminance of about 3356 cdm⁻² at a lower voltage of 13.4 V. Furthermore, these solution-processed devices show decent efficiency data. Compared with other polymeric PHOLEDs, device **A2** shows respectable peak

Table 3. Performance data of polymetallayne-doped electrophosphorescent OLEDs.

Device	Phosphor dopant	$V_{ m turn-on} \ [V]$	Luminance L [cd m ⁻²]	η _{ext} [%]	$\eta_L \\ [cdA^{-1}]$	$\frac{\eta_p}{[LmW^{-1}]}$	λ_{\max} [nm] ^[d]
A1	P1 (5 wt%)	6.4	243 ^[a]	0.39	1.26	0.41	552
			1117 ^[b]	0.35	1.09	0.31	(0.46, 0.52)
			2262 (13.2) ^[c]	0.40 (9.8)	1.26 (9.8)	0.42 (9.2)	
A2	P1 (10 wt%)	5.9	323 ^[a]	0.40	1.57	0.54	552
			1255 ^[b]	0.40	1.28	0.36	(0.47, 0.52)
			3356 (13.4) ^[c]	0.50 (8.8)	1.59 (8.6)	0.60 (7.8)	
A3	P1 (20 wt%)	5.2	81 ^[a]	0.15	0.40	0.18	552
			476 ^[b]	0.16	0.47	0.17	(0.46, 0.52)
			1650 (12.2) ^[c]	0.17 (8.8)	0.48(8.8)	0.18 (7.8)	
B1	P2 (5 wt%)	7.2	276 ^[a]	0.60	1.40	0.40	580
			996 ^[b]	0.43	0.99	0.24	(0.56, 0.43)
			2258 (15.2) ^[c]	0.63 (10.0)	1.45 (10.0)	0.47 (9.4)	
B2	P2 (10 wt%)	5.6	287 ^[a]	0.63	1.47	0.43	580
			1067 ^[b]	0.47	1.08	0.26	(0.56, 0.43)
			2708 (15.4) ^[c]	0.67 (9.4)	1.55 (9.4)	0.55 (8.2)	
B3	P2 (20 wt%)	5.7	123 ^[a]	0.27	0.64	0.23	580
			584 ^[b]	0.26	0.23	0.16	(0.56, 0.44)
			1861 (14.8) ^[c]	0.28 (9.6)	0.65 (9.6)	0.24 (8.0)	

[a] Values collected at 20 mA cm⁻². [b] Values collected at 100 mA cm⁻². [c] Maximum values of the devices. Values in parentheses are the voltages at which they were obtained. [d] CIE coordinates [x, y] in parentheses.

G. Zhou, W.-Y. Wong, Z. Xie, X. Zhao et al.

current efficiency (η_L) of 1.59 cd A⁻¹ at 8.6 V, external quantum efficiency (η_{ext}) of 0.50% at 8.8 V, and power efficiency (η_{P}) of 0.60 $Lm\,W^{-1}$ at 7.8 V. The best efficiencies for device **B2** are defined by $\eta_L = 1.55 \text{ cd } A^{-1}$ at 9.4 V, $\eta_{ext} = 0.67 \%$ at 9.4 V, and $\eta_P = 0.55 \text{ Lm W}^{-1}$ at 8.2 V. These results are somewhat unexpected because binding of the iridium-emitting centers with trans-Pt(PBu₃)₂ moieties should inevitably push the phosphorescent Ir(C^N)₂(acac) sites much closer as compared with the traditional phosphorescent Ir copolymers, in which the phosphorescent cores are more scattered along the polymer backbone in the presence of a higher fraction of the organic components that can avoid the quenching effect among the emitting sites. Instead, the phosphorescent Ir centers tend to get closer to each other in P1 and P2 while the performance data of PHOLEDs prepared with P1 and P2 are still comparable to or even better than some reported data from the devices with traditional phosphorescent copolymers consisting of Ir in the main chain.^[18] In the previous section, the TD-DFT results show that the d_{π} orbitals of Pt have a notable contribution to the HOMO of the oligometallaynes (Table 2). So, the Pt^{II} centers would strengthen the spin-orbit coupling effect to induce their own organic triplet emission, apart from the original phosphorescence arising from the Ir(C^N)2(acac) chromophores. Also, the energy of the triplet state induced by the $\mathsf{P}\mathsf{t}^{\mathrm{II}}$ center is higher than that of the Ir^{III} center on the basis of the photophysical data for the reported Pt^{II}-bis(aryleneethynylene)s.^[19] Thus, there should be an efficient energy transfer from the high-energy triplets induced by the Pt^{II} centers to the low-energy ones by Ir^{III} centers, and hence, only peaks resembling the line shape of the emission of the Ir^{III} phosphorescent centers can be observed in both the PL and EL spectra (Figures 1b and 4 and Figure S2 in the Supporting Information). Such energy transfer process would not only maintain good color purity of the emission but also enhance the phosphorescence intensity of the Ir^{III} center. In other words, there is a synergistic effect between the two different metal centers which can offer better phosphorescence properties. As a result, the performance of PHOLEDs made from the dual metal-centered oligometallaynes is still satisfactory. The present work provides a new platform for designing and synthesizing these organometallic compounds with bimetallic skeletons.

Conclusions

A prominent class of phosphorescent oligometallaynes of dual metal centers (Ir^{III} and Pt^{II}) were designed and synthesized for the first time. Their thermal and photophysical properties were also presented. Theoretical TD-DFT investigation together with their detailed photophysics showed that the emissive species involved in these oligometallaynes mainly arise from the Ir^{III}-centered building block with added benefits endowed by the Pt^{II} component. Experimental results indicated that there is a synergistic effect between the two kinds of metal centers which can improve the phosphorescent characteristics of the bimetallic metallaynes. By virtue of such advantageous synergistic bimetallic effect, these new oligometallaynes possess great potential for simple solution-processed PHOLEDs. These triplet emitters can be further optimized by structural modifications of the C^N ligand groups on $Ir(C^N)_2(acac)$ unit to fine-tune both the device color and efficiency. We believe that the advantages of electrophosphorescence and solution processing that our phosphors offer can be seen as a big step forward in the advance of high-performance solution-processed PHOLEDs.

Experimental Section

General Information

All reactions were performed under a nitrogen atmosphere but no special precautions were required during work-up. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminum plates. Flash column chromatography was carried out using silica gel (200–300 mesh). Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system. The NMR spectra were measured in CDCl₃ on a Bruker AXS 300 or 400 MHz spectrometer with the ¹H and ¹³C chemical shifts quoted relative to tetramethylsilane and ³¹P chemical shifts relative to the 85 % H_3PO_4 external standard.

Physical Measurements

FT-IR spectra for the sample in KBr pellet were recorded on Nicolet Magna-IR 550 Series II spectrometer. UV/Vis spectra were obtained on a Shimadzu UV-2250 spectrophotometer. The photoluminescent properties of the compounds were examined using a Hitachi F-4500 fluorescence spectrophotometer. The phosphorescence quantum yields were determined in degassed CH2Cl2 solutions at 293 K against fac-[Ir(ppy)3] standard $(\Phi_{\rm P}=0.40)$.^[20] The lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a hydrogen-filled pulse lamp as the excitation source. The data analysis was conducted by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit under a nitrogen flow at a heating rate of 10°C min⁻¹. The thermal gravimetric analysis (TGA) was conducted on a NETZSCH STA 409C instrument under nitrogen with the heating rate of 20°C min⁻¹. Gel permeation chromatography (GPC) measurements were carried out on a Waters Breeze system equipped with a Waters 2487 UV/Vis detector and a set of 3 columns (Styragel HR3, HR4E, and HR4) at 30 °C. CHCl3 was used as the mobile phase with a flow rate of 1 mLmin⁻¹. Calibration was performed by using a set of polystyrene standards. Electrochemical measurements were made using a Princeton Applied Research model 273 A potentiostat. The cyclic voltammetry experiment of the sample film was performed at a scan rate of 100 mVs⁻¹ using a eDAQ EA161 potentiostat electrochemical interface equipped with a thin film coated ITO covered glass working electrode, a platinum counter electrode and a Ag/AgCl (in 3M KCl) reference electrode. The solvent in all measurements was deoxygenated MeCN, and the supporting electrolyte was $0.1 \text{ M} [n\text{Bu}_4\text{N}][\text{PF}_6]$. Thin sample films were deposited on the working electrode by dip-coating in chlorobenzene solution (6 mgmL^{-1}). The onset oxidation potential $(E_{\text{onset.ox}})$ and optical bandgap (E_g) were used to determine the HOMO and LUMO energy levels using the equations $E_{\text{HOMO}} = [-(E_{\text{onset,ox} (vs Ag/Ag}))]$ $_{\text{Cl}}-E_{\text{onset (N.H.E. vs Ag/AgCl)}}]-4.50 \text{ eV and } E_{\text{LUMO}}=(E_{\text{HOMO}}+E_{\text{g}}) \text{ eV}, \text{ where the}$ potentials for N.H.E. versus vacuum and N.H.E. versus Ag/AgCl are 4.50 and -0.22 V, respectively.^[21]

General Procedure for the Synthesis of P1 and P2

Under an inert N₂ atmosphere, equimolar amounts of each corresponding metalloligand and *trans*-[Pt(PBu₃)₂Cl₂] were added to a mixture of Et₃N and CH₂Cl₂ (1:1 v/v) with a catalytic amount of CuI. The reaction mixture was stirred at room temperature overnight. Then the reaction mixture was passed through a short silica pad using CH₂Cl₂ as eluent and the volatile components were removed under reduced pressure to get a crude product. A small amount of CH₂Cl₂ was added to dissolve the crude polymetallayne. The solution was then poured into methanol. The orange precipitate formed was collected and dried to get the title oligometallaynes in ~87 % yield.

P1: (Yield: 87%). ¹H NMR (400 MHz, CDCl₃): δ =8.40 (d, br, 2H, Ar), 7.68 (d, br, 2H, Ar), 7.60 (t, br, 2H, Ar), 7.31 (d, br, 2H, Ar), 6.97 (t, br, 2H, Ar), 6.70 (d, br, 2H, Ar), 6.15 (s, br, 2H, Ar), 5.16 (s, br, 1H, acac), 1.88 (br, 12H, PBu₃), 1.76 (s, br, 6H, acac), 1.40 (br, 12H, PBu₃), 1.28 (m, br, 12H, PBu₃), 0.81 ppm (t, br, 18H, PBu₃); ³¹P NMR (161.9 MHz, CDCl₃): δ =4.15 ppm (¹*J*_{P-Pt}=2375 Hz); Gel permeation chromatography (GPC): number-average molecular weight (*M*_n)=1.3×10⁴ gmol⁻¹, poly-dispersity index (PDI)=1.18 (against polystyrene standards).

P2: (Yield: 87%). ¹H NMR (270 MHz, CDCl₃): δ =8.60 (d, br, 2H, Ar), 7.93 (d, br, 2H, Ar), 7.78–7.75 (m, br, 2H, Ar), 7.45 (s, br, 2H, Ar), 7.15–7.04 (m, 8H, Ar), 6.51 (s, br, 2H, Ar), 5.23 (s, br, 1H, acac), 2.13 (br, 12H, PBu₃), 1.90–1.70 (m, 14H, acac and Bu), 1.59 (br, 12H, PBu₃), 1.41 (m, br, 12H, PBu₃), 1.06 (br, 4H, Bu), 0.88 (m, br, 22H, PBu₃ and Bu), 0.69–0.42 ppm (m, 20H, Bu); ³¹P NMR (161.9 MHz, CDCl₃): δ = 3.75 ppm (¹J_{P-Pt}=2355 Hz); GPC: M_n =1.1×10⁴ gmol⁻¹, PDI=1.56 (against polystyrene standards).

OLED Fabrication and Measurements

The pre-cleaned ITO glass substrates were treated with ozone for 20 min. Then, the PEDOT:PSS was deposited on the surface of ITO glass by spin-coating method to form a 40 nm-thick hole-injection layer after being cured at 120°C for 30 min in air. The emitting layer (50 nm) was obtained by spin-coating a chloroform solution of each phosphorescent dopant (*x* wt%) in CBP at various concentrations. The sample was dried in a vacuum oven at 50°C for 15 min and it was transferred to the deposition system for organic and metal deposition. BCP (15 nm), Alq₃ (40 nm), LiF (1 nm) and Al cathode (100 nm) were successively evaporated at a base pressure less than 10⁻⁶ Torr. The EL spectra and CIE coordinates were measured with a PR650 spectra colorimeter. The *L-V-J* curves of the devices were recorded by a Keithley 2400/2000 source meter and the luminance was measured using a PR650 SpectraScan spectrometer. All the experiments and measurements were carried out under ambient conditions.

Computational Details

Density functional theory (DFT) calculations using the B3LYP functional were performed. The basis set used for C, H, N, and O atoms was 6-31G while effective core potentials with a LanL2DZ basis set were employed for P, Pt, and Ir atoms.^[22] Polarization functions were added for P ($\zeta_d(P)=0.340$). All calculations were carried out using the Gaussian 03 program.^[23] Mulliken population analyses were performed using Mull-Pop.^[24] Frontier molecular orbitals obtained from the DFT calculations were plotted using the Molden 3.7 program written by Schaftenaar.^[25]

Acknowledgements

This work was supported by a grant from Xi'an Jiao Tong University (No. 08140004), a Research Grant from Shaanxi Province (No. 2009JQ2008), and the National Natural Science Foundation of China (No. 20902072). W.-Y. Wong thanks the Croucher Foundation for the Croucher Senior Research Fellowship, Hong Kong Baptist University (FRG2/08-09/111), the Hong Kong Research Grants Council (HKBU202508) and a grant from Areas of Excellence Scheme, University Grants Committee, Hong Kong (Project No. [AoE/P-03/08]).

- a) R. Noyori, Angew. Chem. 2002, 114, 2108; Angew. Chem. Int. Ed.
 2002, 41, 2008; b) W.S. Knowles, Angew. Chem. 2002, 114, 2096; Angew. Chem. Int. Ed. 2002, 41, 1998; c) B. Cornils, W. A. Herrmann, M. Muhler, C.-H. Wong, Catalysis from A To Z: A Concise Encyclopedia, Wiley-VCH, Weinheim, 2007; d) R. Sheldon, I. Arends, U. Hanefeld, Green Chemistry and Catalysis, Wiley-VCH, Weinheim, 2007; e) Z. Wang, G. Chen, K. Ding, Chem. Rev. 2009, 109, 322; f) G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, Handbook of Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2008.
- [2] a) A. Coskun, B. T. Baytckin, E. U. Akkaya, *Tetrahedron Lett.* 2003, 44, 5649; b) S. Mizukami, T. Nagono, Y. Urano, A. Odani, K. Kikuchi, *J. Am. Chem. Soc.* 2002, 124, 3920; c) M. Melaimi, F. P. Gabbaï, *J. Am. Chem. Soc.* 2005, 127, 9680; d) R. Martínez-Máñez, F. Sancenón, *Chem. Rev.* 2003, 103, 4419.
- [3] a) A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 2000, 33, 269; b) J.-H. Yum, P. Chen, M. Grätzel, M. K. Nazeeruddin, ChemSusChem 2008, 1, 699; c) H. Imahori, T. Umeyama, S. Ito, Acc. Chem. Res. 2009, 42, 1809; d) P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Grätzel, Nat. Mater. 2003, 2, 402.
- [4] P. W. N. M. van Leeuwen, Homogeneous Catalysis-Understanding the Art, Kluwer Academic Publishers, Dordrecht 2004.
- [5] a) I. Ojima, Catalytic Asymmetric Synthesis, Wiley-VCH, Weinheim, 2000; b) E. N. Jacobsen, A. Pfaltz, H. Yamamoto, Comprehensive Asymmetric Catalysis, Springer, Berlin, 1999.
- [6] a) F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, M. Grätzel, J. Am. Chem. Soc. 2008, 130, 10720; b) W.-Y. Wong, X.-Z. Wang, Z. He, A. B. Djurišić, C.-T. Yip, K.-Y. Cheung, H. Wang, C. S.-K. Mak, W.-K. Chan, Nat. Mater. 2007, 6, 521; c) W.-Y. Wong, X.-Z. Wang, Z. He, K.-K. Chan, A. B. Djurišić, K.-Y. Cheung, C.-T. Yip, A. M.-C. Ng, Y. Y. Xi, C. S.-K. Mak, W.-K. Chan, J. Am. Chem. Soc. 2007, 129, 14372; d) W.-Y. Wong, Macromol. Chem. Phys. 2008, 209, 14; e) L. Liu, C.-L. Ho, W.-Y. Wong, K.-Y. Cheung, M.-K. Fung, W.-T. Lam, A. B. Djurišić, W.-K. Chan, Adv. Funct. Mater. 2008, 18, 2824; f) X.-Z. Wang, W.-Y. Wong, K.-Y. Cheung, M.-K. Fung, A. B. Djurišić, W.-K. Chan, 2008, 5484.
- [7] a) G.-J. Zhou, W.-Y. Wong, Z. Lin, C. Ye, Angew. Chem. 2006, 118, 6335; Angew. Chem. Int. Ed. 2006, 45, 6189; b) G.-J. Zhou, W.-Y. Wong, C. Ye, Z. Lin, Adv. Funct. Mater. 2007, 17, 963; c) G.-J. Zhou, W.-Y. Wong, D. Cui, C. Ye, Chem. Mater. 2005, 17, 5209; d) G.-J. Zhou, W.-Y. Wong, S.-Y. Poon, C. Ye, Z. Lin, Adv. Funct. Mater. 2009, 19, 531; e) F. Guo, W. Sun, Y. Liu, K. Schanze, Inorg. Chem. 2005, 44, 4055; f) W. Sun, H. Zhu, P. M. Barron, Chem. Mater. 2006, 18, 2602; g) R. Vestberg, R. Westlund, A. Eriksson, C. Lopes, M. Carlsson, B. Eliasson, E. Glimsdal, M. Lindgren, E. Malmström, Macromolecules 2006, 39, 2238; h) R. Westlund, E. Malmström, C. Lopes, J. Öhgren, T. Rodgers, Y. Saito, S. Kawata, E. Glimsdal, M. Lindgren, Adv. Funct. Mater. 2008, 18, 1939; i) R. Zieba, C. Desroches, F. Chaput, M. Carlsson, B. Eliasson, B. Eliasson, C. Lopes, M. Lindgren, S. Parola, Adv. Funct. Mater. 2009, 19, 235.
- [8] a) C.-H. Yang, Y.-M. Cheng, Y. Chi, C.-J. Hsu, F.-C. Fang, K.-T. Wong, P.-T. Chou, C.-H. Chang, M.-H. Tsai, C.-C. Wu, Angew. Chem. 2007, 119, 2470; Angew. Chem. Int. Ed. 2007, 46, 2418; b) C.-L. Li, Y.-J. Su, Y.-T. Tao, P.-T. Chou, C.-H. Chien, C.-C. Cheng, R.-S. Liu, Adv. Funct. Mater. 2005, 15, 387; c) C.-F. Chang, Y.-M. Cheng, Y. Chi, Y.-C. Chiu, C.-C. Lin, G.-H. Lee, P.-T. Chou, C.-C. Chen, C.-H. Chang, C.-C. Wu, Angew. Chem. 2008, 120, 4618; Angew. Chem. Int. Ed. 2008, 47, 4542; d) Y.-H. Song, S.-J. Yeh, C.-T. Chen, Y. Chi, C.-S. Liu, J.-K. Yu, Y.-H. Hu, P.-T. Chou, S.-M. Peng, G.-H. Lee, Adv. Funct. Mater. 2004, 14, 1221; e) S. Bettington, M. Tavasli, M. R. Bryce, A. Beeby, H. Al-Attar, A. P. Monkman, Chem. Eur. J. 2007, 13, 1423; f) J. M. Lupton, I. D. W. Samuel, M. J. Frampton, R. Beavington, P. L. Burn, Adv. Funct. Mater. 2001, 11, 287; g) C.-L. Lee, R. R. Das, J.-J. Kim. Chem. Mater. 2004, 16, 4642; h) M. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Grätzel, J. Am. Chem. Soc. 2003, 125, 8790; i) Y. Chi, P.-T. Chou, Chem. Soc. Rev. 2010, 39, 638; j) P.-T. Chou, Y. Chi, Eur. J. Inorg. Chem. 2006, 3319; k) P.-T. Chou, Y. Chi, Chem. Eur. J. 2007, 13, 380; l) Y. You, S. Y. Park, Dalton Trans. 2009, 1267.

- [9] a) C.-M. Che, S.-C. Chan, H.-F. Xiang, M. C. W. Chan, Y. Liu, Y. Wang, *Chem. Commun.* 2004, 1484; b) M. Cocchi, D. Virgili, V. Fattori, D. L. Rochester, J. A. G. Williams, *Adv. Funct. Mater.* 2007, *17*, 285; c) S.-C. Chan, M. C. W. Chan, Y. Wang, C.-M. Che, K.-K. Cheung, N. Zhu, *Chem. Eur. J.* 2001, 7, 4180; d) J. Kavitha, S.-Y. Chang, Y. Chi, J.-K. Yu, Y.-H. Hu, P.-T. Chou, S.-M. Peng, G.-H. Lee, Y.-T. Tao, C.-H. Chien, A. J. Carty, *Adv. Funct. Mater.* 2005, *15*, 223; e) W.-Y. Wong, Z. He, S.-K. So, K.-L. Tong, Z. Lin, *Organometallics* 2005, *24*, 4079; f) G.-J. Zhou, X.-Z. Wang, W.-Y. Wong, X.-M. Yu, H.-S. Kwok, Z.-Y. Lin, *J. Organomet. Chem.* 2007, *692*, 3461; g) C. Yang, X. Zhang, H. You, L. Zhu, L. Chen, L. Zhu, Y. Tao, D. Ma, Z. Shuai, J. Qin, *Adv. Funct. Mater.* 2007, *17*, 651; h) G. Zhou, Q. Wang, C.-L. Ho, W.-Y. Wong, D. Ma, L. Wang, *Chem. Commun.* 2009, 3574; i) C.-L. Ho, W.-Y. Wong, B. Yao, Z. Xie, L. Wang, Z. Lin, *J. Organomet. Chem.* 2009, 694, 2735.
- [10] a) Y.-H. Niu, Y.-L. Tung, Y. Chi, C.-F. Shu, J. H. Kim, B. Chen, J. Luo, A. J. Carty, A. K.-Y. Jen, *Chem. Mater.* 2005, *17*, 3532; b) X. Jiang, A. K.-Y. Jen, B. Carlson, L. R. Dalton, *Appl. Phys. Lett.* 2002, *81*, 3125; c) B. Carlson, G. D. Phelan, W. Kaminsky, L. Dalton, X. Z. Jiang, S. Liu, A. K.-Y. Jen, *J. Am. Chem. Soc.* 2002, *124*, 14162; d) S. Bernhard, X. Gao, G. G. Malliaras, H. D. Abruna, *Adv. Mater.* 2002, *14*, 433; e) Y. Ma, H. Zhang, J. Shen, C. Che, *Synth. Met.* 1998, *94*, 245; f) Y.-L. Tung, S.-W. Lee, Y. Chi, Y.-T. Tao, C.-H. Chien, Y.-M. Cheng, P.-T. Chou, S.-M. Peng, C.-S. Liu, *J. Mater. Chem.* 2005, *15*, 460.
- [11] a) M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, Y. Taga, Appl. Phys. Lett. 2001, 79, 156; b) W.-Y. Wong, G.-J. Zhou, X.-M. Yu, H.-S. Kwok, B.-Z. Tang, Adv. Funct. Mater. 2006, 16, 838; c) W.-Y. Wong, C.-L. Ho, Z.-Q. Gao, B.-X. Mi, C.-H. Chen, K.-W. Cheah Z. Lin, Angew. Chem. 2006, 118, 7964; Angew. Chem. Int. Ed. 2006, 45, 7800; d) G.-J. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D.-G. Ma, L.-X. Wang, Z.-Y. Lin, T. B. Marder, A. Beeby, Adv. Funct. Mater. 2008, 18, 499; e) G.-J. Zhou, W.-Y. Wong, B. Yao, Z.-Y. Xie, L.-X. Wang, Angew. Chem. 2007, 119, 1167; Angew. Chem. Int. Ed. 2007, 46, 1149; f) G.-J. Zhou, W.-Y. Wong, B. Yao, Z.-Y. Xie, L.-X. Wang, J. Mater. Chem. 2008, 18, 1799; g) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, J. Am. Chem. Soc. 2001, 123, 4304; h) A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, J. Am. Chem. Soc. 2003, 125, 12971; i) W.-Y. Wong, C.-L. Ho, J. Mater. Chem. 2009, 19, 4457; j) W.-Y. Wong, C.-L. Ho, Coord. Chem. Rev. 2009, 253, 1709.
- [12] a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* 1998, 395, 151; b) M. A. Baldo, M. E. Thompson, S. R. Forrest, *Nature* 2000, 403, 750; c) H. Yersin, *Top. Curr. Chem.* 2004, 241, 1.
- [13] a) M. Shiotsuka, Y. Yamamoto, S. Okuno, M. Kitou, K. Nozaki, S. Onaka, Chem. Commun. 2002, 590; b) I. E. Pomestchenko, D. E. Polyansky, F. N. Castellano, Inorg. Chem. 2005, 44, 3412; c) K.-H. Chang, C.-C. Huang, Y.-H. Liu, Y.-H. Hu, P.-T. Chou, Y.-C. Lin, Dalton Trans. 2004, 1731; d) J. Vicente, M.-T. Chicote, M. M. Alvar-ez-Falcón, Organometallics 2005, 24, 2764; e) O. Lavastre, M. Even, P. H. Dixneuf, A. Pacreau, J.-P. Vairon, Organometallics 1996, 15, 1530; f) N. J. Long, A. J. Martin, R. Vilar, A. J. P. White, D. J. Williams, M. Younus, Organometallics 1999, 18, 4261; g) K.-L. Cheung, S.-K. Yip, V. W.-W. Yam, J. Organomet. Chem. 2004, 689, 4451; h) S. C.-F. Lam, V. W.-W. Yam, K. M.-C. Wong, E. C.-C. Cheng, N. Zhu, Organometallics 2005, 24, 4298; i) W.-Y. Wong, W.-K. Wong, P. R. Raithby, J. Chem. Soc. Dalton Trans. 1998, 2761; j) K. Liu, C.-

L. Ho, S. Aouba, Y.-Q. Zhao, Z.-H. Lu, S. Petrov, N. Coombs, P. Dube, H. E. Ruda, W.-Y. Wong, I. Manners, *Angew. Chem.* **2008**, *120*, 1275; *Angew. Chem. Int. Ed.* **2008**, *47*, 1255.

- [14] a) J. K. Stille, Angew. Chem. 1986, 98, 504; Angew. Chem. Int. Ed. Engl. 1986, 25, 508; b) K. Sonogashira in Comprehensive Organic Synthesis, Vol. 3 (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, UK, 1991, p. 551; c) F. Diederich, P. J. Stang, R. R. Tykwinski, Acetylene Chemistry, Wiley-VCH, Weinheim, 2005.
- [15] a) Y. Fujikura, K. Sonogashira, N. Hagihara, *Chem. Lett.* 1975, 1067;
 b) K. Sonogashira, S. Takahashi, N. Hagihara, *Macromolecules* 1977, 10, 879;
 c) W.-Y. Wong, G.-L. Lu, K.-H. Choi, J.-X. Shi, *Macromolecules* 2002, 35, 3506.
- [16] a) L. A. Emmert, W. Choi, J. A. Marshall, J. Yang, L. A. Meyer, J. A. Brozik, *J. Phys. Chem. A* 2003, *107*, 11340; b) S. M. Aly, C.-L. Ho, D. Fortin, W.-Y. Wong, A. S. Abd-El-Aziz, P. D. Harvey, *Chem. Eur. J.* 2008, *14*, 8341; c) S. M. Aly, C.-L. Ho, W.-Y. Wong, D. Fortin, P. D. Harvey, *Macromolecules* 2009, *42*, 6902.
- [17] a) S. P. McGlynn, F. J. Smith, G. Cilento, *Photochem. Photobiol.* **1964**, *3*, 269; b) J. E. Rogers, T. M. Cooper, P. A. Fleitz, D. J. Glass, D. G. McLean, *J. Phys. Chem. A* **2002**, *106*, 10108.
- [18] a) Y. Zhang, Y. Xu, Q. Niu, J. Peng, W. Yang, X. Zhu, Y. Cao, J. Mater. Chem. 2007, 17, 992; b) H. Zhen, C. Jiang, W. Yang, J. Jiang, F. Huang, Y. Cao, Chem. Eur. J. 2005, 11, 5007; c) Q. Zhao, S.-J. Liu, W. Huang, Macromol. Rapid Commun. 2010, 31, 794; d) J. Jiang, W. Yang, Y. Cao, J. Inorg. Organomet. Polym. Mater. 2007, 17, 37.
- [19] a) W.-Y. Wong, Coord. Chem. Rev. 2006, 250, 2627; b) W.-Y. Wong, Dalton Trans. 2007, 4495; c) W.-Y. Wong, P. D. Harvey, Macromol. Rapid Commun. 2010, 31, 671.
- [20] K. A. King, P. J. Spellane, R.-J. Watts, J. Am. Chem. Soc. 1985, 107, 1431.
- [21] a) J. Hou, Z. Tan, Y. Yan, Y. He, C. Yang, Y. Li, J. Am. Chem. Soc. 2006, 128, 4911; b) C. G. Van de Walle, J. Neugebauer, Nature 2003, 423, 626.
- [22] a) W. R. Wadt, P. J. Hay, J. Chem. Phys. 1985, 82, 284; b) P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 299.
- [23] Gaussian 03, revision B05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 2003.
- [24] *MullPop*, a program written by Reinaldo Pis Diez at the National University of La Plata, Argentina.
- [25] G. Schaftenaar Molden v3.7; CAOS/CAMM Center Nijmegen: Toernooiveld, Nijmegen, Netherlands, 2001.

Received: May 10, 2010 Revised: June 7, 2010 Published online: September 3, 2010