Tris-Cyclometalated Iridium(III) Styryl Complexes and Their Saturated Analogues: Direct Functionalization of Ir(4-Me-ppy)$_3$ and Hydrogen Transfer Process

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Received May 13, 2005

Summary: A new series of tris-cyclometalated Ir(III) styryl complexes and their saturated analogues have been synthesized; the former are formed by functionalization of Ir(4-Me-ppy)$_3$ and the latter from a hydrogen transfer process to the styryl groups. Their luminescence properties have been investigated.

Introduction

Cyclometalated iridium(III) complexes have been used for the preparation of OLEDs, due to their high phosphorescence efficiencies and multicolor emission.[1] The phosphorescence strongly depends on the nature of the cyclometalating ligand (C∧N). Ir(C∧N-ppy)$_3$ (ppy = phenylpyridine) is one of the representative complexes, and many heterocycles have been also used as the C∧N ligand.[2] A systematic functionalization of the pyridine ring has not been reported so far;[3] that is why we have developed a simple procedure to functionalize the para position of the pyridine ring of 4-methyl-2-phenylpyridine (4-Me-ppy), allowing the introduction of various conjugated groups. Through this synthetic flexibility, the electronic properties, i.e., absorption and emission properties, can be tuned by modification of the end group and/or the nature of the linker, allowing the rational design of phosphor emitters.

We report here the synthesis, spectroscopic characterization, and photophysical properties of a new series of tris-cyclometalated Ir(III) styryl complexes and their saturated analogues. We point out the hydrogen transfer process to the styryl groups occurring during the course of the synthesis. This prompted us to develop an alternative route by direct functionalization of the Ir(4-Me-ppy)$_3$ complex. This strategy has never been reported for tris-chelate Ir complexes and allows us to produce the desired unsaturated species in good yields, the luminescence properties of which will be described.

Results and Discussion

The tris-cyclometalated iridium complexes Ir(C∧N)$_3$ are generally synthesized from the corresponding bis-cyclometalated chloro-bridged dimers, and depending on the reaction temperature and the nature of the ligand, the fac or mer isomer can be obtained.[4] This approach was applied to 4-substituted-styryl 2-phenylpyridines, 4-(4-methoxystyryl)- and 4-(4-(diethylamino)styryl)-2-phenylpyridine (ppy-4-styryl-R: **1a**, R = OMe; **1b**, R = NEt$_2$).[5] The precursor dimers [Ir(C∧N-ppy-4-styryl-R)$_2$]$_2$-(μ-Cl)$_2$ (**2a**, R = OMe; **2b**, R = NEt$_2$) were prepared from IrCl$_3$·nH$_2$O with an excess of the appropriate HC∧N ligand (140 °C, 2-ethoxyethanol/H$_2$O).[6] Dimers **2a**,**b** were isolated as orange-red powders that were sparingly soluble in CH$_2$Cl$_2$. As previously reported, due to the strong trans effect, only the C,C-cis isomer was obtained.[7] The ^{1}H NMR spectra of crude **2a**,**b** revealed only one set of signals, which were attributed to the racemic mixture (ΔΔ/ΛΛ), as indicated by a characteristic low-field doublet at δ 9.10 for the pyridine proton in the 6-position. The synthesis of the corresponding tris-cyclometalated complexes was then attempted by reacting **2a**,**b** with ligands **1a**,**b**, respectively, in refluxing glycerol in the presence of sodium carbonate. Remarkably, treatment of **2a** with **1a** afforded the

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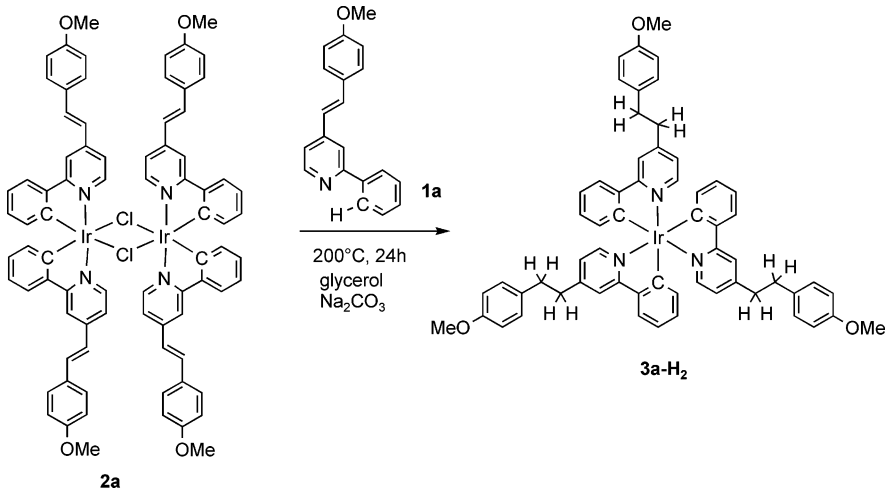
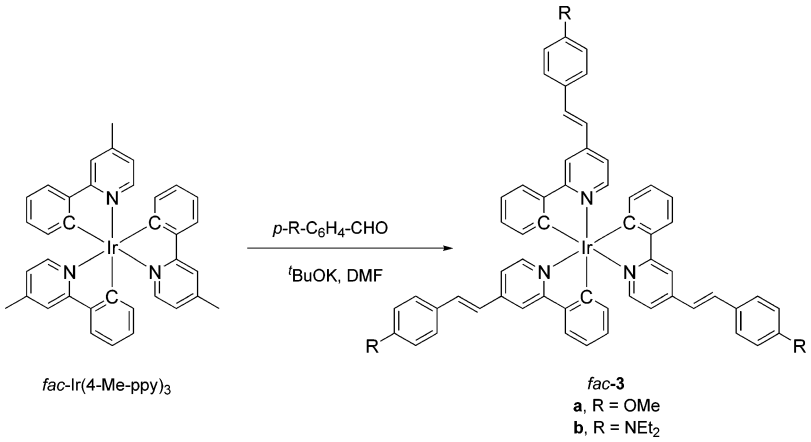
10.1021/om050383f CCC: $30.25
Publication on Web 10/19/2005

Scheme 1



Scheme 2



saturated complex *fac*-**3a-H**$_2$ (Scheme 1). Indeed, ^{1}H NMR spectroscopic data clearly indicated that the C=C double bond of the styryl groups of the coordinated C∧N ligands and that of the incoming ligand **1a** were fully hydrogenated under the reaction conditions used. The characteristic AB signal of the styryl group vanished, and the methylene protons appeared as multiplets at δ 3.00 and 2.95. The $^{13}C\{^1H\}$ NMR spectrum exhibited two resonances at δ 37.8 and 35.8 for the CH_2 groups, in agreement with the proposed structure. In contrast, reaction of **2b** with the NEt_2-containing ligand **1b** did not give the corresponding tris-cyclometalated complex; instead, the free hydrogenated ligand **1b-H**$_2$ was isolated. It is noteworthy that the preparation of tris-chelate species is generally difficult to achieve and not always effective, as the third C−H ortho-metalation process requires very severe conditions, leading to side reactions.[2e]

We assume that the formation of *fac*-**3a-H**$_2$ results from a catalytic transfer hydrogenation of the styryl groups involving Ir species. Such a process, which requires a hydrogen donor (usually an alcohol) and a base, could be operative under the reaction conditions used (glycerol and sodium carbonate).[8] In line with this proposal, we found that the dimer $[Ir(C\wedge N\text{-}ppy)_2]_2(\mu\text{-}Cl)_2$ (5 mol %) catalyzes the conversion of the free styryl ligand **1a** under the very drastic reaction conditions (glycerol, Na_2CO_3, 200 °C); **1a-H**$_2$ is quantitatively formed.[9]

The styryl-containing complexes are alternately prepared by direct functionalization of Ir complexes.[10] Specifically, the tris-chelate methyl complex *fac*-Ir(4-Me-ppy)$_3$ was treated at room temperature with the appropriate *p*-R-benzaldehyde in the presence of ^{t}BuOK. Under these reaction conditions, the unsaturated complexes *fac*-**3a,b** were obtained as red powders in good yield (Scheme 2). For instance, the *trans*-styryl group in *fac*-**3a** was characterized in the ^{1}H NMR spectrum by an AB system located at δ 7.36 and 7.02 (^3J = 16 Hz) and signals at δ 133.4 and 123.2 in the $^{13}C\{^1H\}$ NMR spectrum.

The absorption spectrum of **3a** shows a strong absorption band at 328 nm characteristic of the intraligand charge transfer (ILCT) from the electron-donor methoxy substituent to the acceptor pyridine ring via the π-linker styryl group (Figure 1). Strikingly, this value is very

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(9) The catalytic transfer hydrogenation of substituted alkenes is not an easy task. For instance, although conversion of *trans*-stilbene into 1,2-diphenylethane has been observed by using hydrido(methoxo)-iridium complexes (MeOH−$PhCH_3$, 80 °C, 18 h), the spectroscopic yield (29%) is quite low; see: Tani, K.; Iseki, A.; Yamagata, T. *Chem. Commun.* **1999**, 1821.

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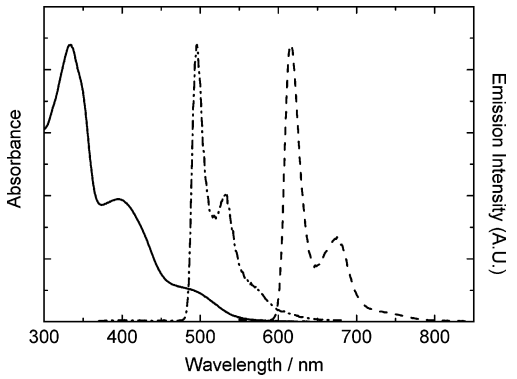

Figure 1. UV−vis absorption spectrum of the complex *fac*-**3a** (—) in Me-THF (298 K) and emission spectra ($\lambda_{exc} = 350$ nm) of the complexes *fac*-**3a** (- - -) and *fac*-**3a**−$\mathbf{H}_2$ (— · —) in CH_2Cl_2/EtOH/MeOH (1:4:1, v/v/v) (77 K), respectively.

similar to that of the free ligand **1a** (325 nm) and is blue-shifted compared to that of the related dimer **2a** (375 nm). The acceptor properties of the pyridine ring are expected to be enhanced by the coordination to the metal,[5] but the strong trans influence of the phenyl ligands in **3a** counterbalances this effect in the facial isomer. At lower energy, the absorption bands (from 400 nm) can be assigned to a combination of singlet and triplet MLCT (d(π) Ir → π^* C∧N) transitions.[2f,4a]

The styryl complex *fac*-**3a** shows very weak emission in CH_2Cl_2 at 298 K ($\lambda_{max} = 526$ nm, $\Phi = 0.0005$, $\tau_0 = 0.96$ μs), but it is emissive in frozen glasses at 77 K ($\lambda_{max} = 616$ nm, $\tau_0 = 3.8$ μs) (Figure 1). The low emission intensity at room temperature could be due to the quenching properties of the *trans*-styryl moiety.[11] The presence of the extented π-conjugation and/or strong intramolecular donor−acceptor interaction into the ligand induces a strong red shift from 298 to 77 K. A bathochromic shift is also observed in comparison to the saturated complex. The complex *fac*-**3a-H**$_2$ is strongly emissive in CH_2Cl_2 solution at room temperature and exhibits, upon excitation, intense and long-lived green phosphorescence with high quantum yield (λ_{max}(298 K) = 509 nm, $\Phi = 0.54$, $\tau_0 = 1.4$ μs; λ_{max}(77 K) = 496 nm) (Figure 1). These data suggest that the emission origins of both complexes are different at 77 K. The emissive state *fac*-**3a-H**$_2$ is likely to be ^{3}MLCT (d(π) Ir → π^* C∧N) in nature,[4,12] whereas the low-energy emission of *fac*-**3a** at 77 K appears to originate from an excited state of triplet intraligand charge transfer (^{3}ILCT) character, in view of a better conjugation between the donor and acceptor groups.

We have discovered a synthetic route to a new series of luminescent tris-cyclometalated Ir(III) complexes, allowing the introduction of functional groups under mild conditions. This promising method avoids the difficult preparation and purification of the tris-chelate complexes. Studies of other functionalized Ir complexes, including their emission properties, will be developed. In addition, these complexes, possessing D_3 symmetry, represent a new class of neutral octupolar NLO-phores.[13] The ability to prepare selectively the styryl-containing complex *fac*-**3** and the corresponding saturated analogue *fac*-**3-H**$_2$ allows a study of the influence of the ILCT vs MLCT transition with regard to NLO activity.

Experimental Section

All manipulations were performed using Schlenk techniques under an Ar atmosphere, but the workups were carried out in air. All solvents were dried and purified by standard procedures. All starting materials were used as received. Ir complexes of 4-Me-ppy (4-methyl-2-phenylpyridine) were prepared by following the literature procedure.[4b] NMR spectra were recorded on Bruker DPX-200, AV 300, and AV 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given versus $SiMe_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Attribution of carbon atoms was based on HMBC, HMQC, and COSY experiments. UV/vis absorption spectra were recorded using a UVIKON 9413 spectrophotometer, and emission spectra were measured on a PTI C 60 fluorescence spectrophotometer. High-resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes, France. Elemental analyses were performed by the Service central d'analyse du CNRS at Vernaison, France. Luminescence quantum yields were measured by the optically dilute method[14] using quinine sulfate in aerated 1.0 N H_2SO_4 ($\Phi_{em} = 0.546$)[14] or an aerated aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\Phi_{em} = 0.028$)[15] as the standard solution. Low-temperature (77 K) glass photophysical measurements were performed with the sample loaded in a quartz tube inside a quartz-walled Dewar flask filled with liquid nitrogen. The excitation source for emission lifetime measurements was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser. Luminescence decay signals from a Hamamatsu R928 photomultiplier tube were converted to potential changes by a 50 Ω load resistor and then recorded on a Tektronix Model TDS 620A digital oscilloscope.

Syntheses of the Chloro-Bridged Dimers [Ir(C∧N-ppy-4-styryl-R)$_2$]$_2$(μ-Cl)$_2$ (2a,b). A Schlenk flask was charged with $IrCl_3 \cdot 3H_2O$ (0.82 mmol), the appropriate ligand HC∧N, **1a**,**b** (3.5 equiv), and 10 mL of a 75:25 mixture of 2-ethoxyethanol and water. The mixture was refluxed for 24 h. The precipitate was then washed with water, ethanol, and acetone. **2a**: red powder; yield 82%. ^{1}H NMR (500 MHz, CD_2Cl_2): 9.15 (d, ^3J = 5.9 Hz, 4H, Py^6), 7.94 (s, 4H, Py^3), 7.62 (d, ^3J = 7.5 Hz, 4H, Ph), 7.39 (m, 12H, =CH and C_6H_4), 7.12 (d, ^3J = 16 Hz, 4H, =CH), 6.93 (d, 4H, Py^5), 6.82 (m, 12H, C_6H_4 and Ph), 6.32 (t, ^3J = 6.8 Hz, 4H, Ph), 6.02 (d, ^3J = 8.0 Hz, 4H, Ph), 3.85 (s, 12H, OCH_3). HRMS: *m/z* 1565.3893 [M − Cl]$^+$, calcd for $C_{80}H_{62}N_4O_4{}^{193}Ir_2Cl_2$ 1565.3876. **2b**: red powder; yield 94%. ^{1}H NMR (500 MHz, $CDCl_3$): 9.10 (d, ^3J = 6 Hz, 4H, Py^6), 7.88 (s, 4H, Py^3), 7.58 (d, 4H, Py^5), 7.44 (d, ^3J = 8.6 Hz, 8H, C_6H_4), 7.38 (d, ^3J = 16 Hz, 4H, =CH), 7.02 (d, ^3J = 16 Hz, 4H, =CH), 6.86 (d, 4H, Ph), 6.77 (t, ^3J = 7.0 Hz, 4H, Ph), 6.68 (d, ^3J = 8.6 Hz, 8H, C_6H_4), 6.60 (t, 4H, Ph), 6.14 (d, ^3J = 7.0 Hz, 4H, Ph), 3.48 (q, ^3J = 6.8 Hz, 16H, CH_2), 1.27 (t, ^3J = 6.8 Hz, 24H, CH_3). HRMS: *m/z* 1729.6435 [M − Cl]$^+$, calcd for $C_{92}H_{92}N_8{}^{193}Ir_2Cl_2$ 1729.6396.

Synthesis of *fac*-3a-H$_2$. In a Schlenk tube, the chloro-bridged dimer **2a** (100 mg, 0.06 mmol), **1a** (45 mg, 0.15 mmol), and Na_2CO_3 (66 mg, 0.62 mmol) were introduced into 10 mL of glycerol. The reaction mixture was heated at 200 °C for 24 h. The precipitate was washed with water (2 × 10 mL), MeOH,

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and diethyl ether. Extraction with CH_2Cl_2, filtration over a pad of SiO_2, and precipitation with Et_2O gave a red powder. Crystallization in a CH_2Cl_2/Et_2O mixture gave 50 mg (38%) of *fac*-**3a-H$_2$**. ^{1}H NMR (500 MHz, CD_2Cl_2): 7.76 (s, 3H, Py^3), 7.67 (d, ^3J = 7.9 Hz, 3H, Ph^3), 7.42 (d, ^3J = 5.6 Hz, 3H, Py^6), 7.14 (d, ^3J = 8.6 Hz, 6H, C_6H_4), 6.91 (td, ^3J = 7 Hz, ^4J = 1.5 Hz, 3H, Ph^4), 6.85 (d, ^3J = 8.6 Hz, 6H, C_6H_4), 6.81 (td, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 3H, Ph^5), 6.78 (m, 6H, Py^5 and Ph^6), 3.80 (s, 9H, OMe), 3.00 (m, 6H, CH_2), 2.95 (m, 6H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): 166.1 (C^2 Py), 161.4 (C^1 Ph), 158.1 (C_6H_4), 151.8 (C^4 Py), 146.6 (C^6 Py), 144.0 (C^2 Ph), 136.7 (C^6 Ph), 132.9 (C_6H_4), 129.3 (C_6H_4, C^5 Ph), 123.8 (C^3 Ph), 122.5 (C^5 Py), 119.6 (C^4 Ph), 118.8 (C^3 Py), 113.8 (C_6H_4), 55.2 (OMe), 37.5 (CH_2), 35.5 (CH_2). HRMS: *m/z* 1057.3818 [*M*]$^+$, calcd for $C_{60}H_{54}N_3O_3{}^{193}$Ir 1057.3800.

Synthesis of *fac*-3a,b. In a Schlenk tube, to a solution of *fac*-Ir(C∧N-ppy-4-Me)$_3$ (160 mg, 0.23 mmol) in 20 mL of DMF, were added *p*-R-benzaldehyde (0.92 mmol) and ^{t}BuOK (103 mg, 0.92 mmol). The reaction mixture was stirred at room temperature for 3 h. Addition of 20 mL of water allowed precipitation of an orange-red powder. The precipitate was filtered off and washed with MeOH and Et_2O. The solid was dried under vacuum (160 mg, 66%). ***fac*-3a**: orange powder; 66% yield. ^{1}H NMR (500 MHz, CD_2Cl_2): 8.01 (br s, 3H, Py^3), 7.79 (d, ^3J = 8 Hz, 3H, Ph^3), 7.62 (d, ^3J = 6 Hz, 3H, Py^6), 7.56 (d, ^3J = 8.8 Hz,6H, C_6H_4), 7.36 (d, ^3J = 16.3 Hz, 3H, =CH), 7.08 (dd, ^3J = 6.0 Hz, ^4J = 1.4 Hz, 3H, Py^5), 7.02 (d, ^3J = 16.3 Hz, 3H, =CH), 6.97 (d, ^3J = 8.8 Hz, 6H, C_6H_4), 6.94 (m, 3H, Ph^4), 6.84 (m, 6H, Ph^5 and Ph^6), 3.87 (s, 6H, OCH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): 166.4 (C^2 Py), 161.3 (C^1 Ph), 160.4 (C^1 C_6H_4), 147.0 (C^6 Py), 145.2 (C^4 Py), 143.9 (C^2 Ph), 136.8 (C^6 Ph), 133.4 (=CH), 129.6 (C^5 Ph), 128.8 (C^4 C_6H_4), 128.5 (C^3 C_6H_4), 123.9 (C^3 Ph), 123.2 (=CH), 119.8 (C^4 Ph), 119.0 (C^5 Py), 115.8 (C^3 Py), 114.2 (C^2 C_6H_4), 55.3 (OCH_3). HRMS: *m/z* 1051.3353 [*M*]$^+$, calcd for $C_{60}H_{48}N_3O_2{}^{193}$Ir 1051.3330. Anal. Calcd for $C_{60}H_{48}N_3O_3Ir\cdot 3CH_2Cl_2$: C, 57.94; H, 4.17; N, 3.22. Found: C, 57.55; H, 4.17; N, 3.22. **3b**: red powder; 43% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): 7.96 (br s, 3H, Py^3), 7.78 (d, ^3J = 7.7 Hz, 3H, Ph^3), 7.57 (d, ^3J = 6 Hz, 3H, Py^6), 7.45 (d, ^3J = 8.8 Hz,6H, C_6H_4), 7.31 (d, ^3J = 16.1 Hz, 3H, =CH), 7.04 (dd, ^3J = 6.0 Hz, ^4J = 1.1 Hz, 3H, Py^5), 6.89 (m, 12H, Ph^4, Ph^5, Ph^6, and =CH), 6.70 (d, ^3J = 8.8 Hz, 6H, C_6H_4), 3.43 (q, ^3J = 6.8 Hz, 12H, CH_2), 1.21 (t, ^3J = 6.8 Hz, 18H, CH_3). HRMS: *m/z* 1174.5246 [*M*]$^+$, calcd for $C_{69}H_{69}N_6{}^{193}$Ir 1174.5213. Anal. Calcd for $C_{69}H_{69}N_6Ir\cdot 2H_2O$: C, 68.46; H, 6.08; N, 6.94. Found: C, 68.78; H, 5.76; N, 7.17.

Synthesis of 1a-H$_2$. Compound **1a** (150 mg, 0.52 mmol), Na_2CO_3 (550 mg, 5.2 mmol), and [Ir(C∧N-ppy)$_2$(μ-Cl)]$_2$ (28 mg, 0.026 mmol) were refluxed at 200 °C in glycerol (20 mL) for 48 h. After the mixture was cooled to room temperature, distilled water (20 mL) was added and the resulting precipitate was filtered off. **1a-H$_2$** was extracted from the residue with methanol and diethyl ether and was isolated as a yellow oil (148 mg, 98%). ^{1}H NMR (200 MHz, $CDCl_3$): 8.57 (d, ^3J = 5 Hz, 1H, Py^6), 7.93 (m, 2H, Ph ortho), 7.46 (m, 4H, Ph meta and para, Py^3), 7.08 (m, 3H, Py^5 and C_6H_4), 6.86 (d, ^3J = 8.8 Hz, 2H, C_6H_4), 3.81 (s, 3H, OCH_3), 2.96 (m, 4H, CH_2). HRMS: *m/z* 289.1455 [*M*]$^+$, calcd for $C_{19}H_{19}NO$ 289.1467.

Acknowledgment. We acknowledge the award of a grant by the CNRS/RGC under the PROCORE: France-Hong Kong Joint Research Scheme. We thank la Région Bretagne for a grant to M.L. Prof. Vivian W.-W. Yam of The University of Hong Kong is gratefully acknowledged for access to equipment for photophysical measurements.

Note Added after ASAP Publication. In the version of this paper posted on the Web Oct 19, 2005, one of the corresponding authors was not indicated with an asterisk. The corresponding author designations that now appear are correct.

OM050383F