Synthesis and characterization of luminescent osmium(II) carbonyl complexes based on chelating dibenzoylmethanate and halide ligands†

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Octahedral Os(II) complexes **1–5** with formula [Os(CO)$_3$X(dbm)] are prepared through utilization of both solid-state pyrolysis and ligand exchange reactions. These complexes exhibit prominent $^3\pi$–π^* phosphorescence with unusually long lifetimes (29–64 μs) and high quantum yields (0.08–0.13).

Photophysical studies of Re(I) tricarbonyl complexes with structural formula *fac*-[Re(CO)$_3$X(L)], X = halides and L = bidentate heterocycles such as 2,2′-bipyridine, have received considerable attention during the last decade.[1] These metal complexes exhibit either low-lying intraligand π–π^* or metal-to-ligand charge transfer (MLCT) absorptions, while the strong emission originates from the excited states with considerable triplet–singlet mixing as a result of enhanced spin–orbit coupling. More recently, these Re(I) metal fragments have been extensively used as the basic building blocks to construct supramolecular transition-metal complexes that may serve as model systems for photoresponsive molecular devices.[2] Interestingly, extension to the missing Os(CO)$_3$X analogues has never been realized possibly due to the lack of a suitable molecular design, resulting in an abrupt discontinuation of this class of highly luminescent metal carbonyl complexes. In this paper, a new series of Os$^{(II)}$(CO)$_3$X are prepared, in which the skeletal arrangement consists of one β-diketonate chromophore such as (dbm)H = dibenzoylmethane to balance the +2 formal charge on the metal, one anionic ligand X and three orthogonal CO ligands located at the octahedral coordination site.

L = 2,2′-bipyridine
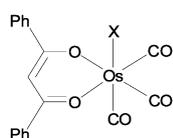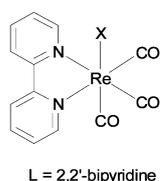
X = CF₃CO₂ (**1**), Cl (**2**)
Br (**3**), I (**4**), & SCN (**5**)

Accordingly, our first target complex [Os(CO)$_3$(tfa)(dbm)] (**1**) was prepared by heating the Os dimer complex [Os$_2$(CO)$_6$(tfa)$_2$][3] (tfa = CF$_3$CO$_2^-$) and a slight excess of dibenzoylmethane (dbm)H in a Carius tube. This solid-state pyrolysis allowed us to conduct the experiments at higher temperatures and to avoid the usage of solvents that may interfere with the reactions.[4]
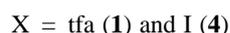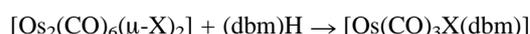
$$[Os_2(CO)_6(\mu\text{-}X)_2] + (dbm)H \rightarrow [Os(CO)_3X(dbm)]$$

$$X = tfa\ (\textbf{1})\ and\ I\ (\textbf{4})$$

$$(\textbf{1}) + NaCl, NaBr\ or\ NH_4SCN \rightarrow [Os(CO)_3X(dbm)]$$

X = Cl (**2**), Br (**3**) and SCN (**5**)

Based on the tfa complex **1**, other related derivatives with X = Cl (**2**), Br (**3**) and SCN (**5**) can be synthesized using simple ligand substitution conducted in refluxing methanol. The only exception is the iodide complex [Os(CO)$_3$I(dbm)] (**4**), which was alternatively prepared using the aforementioned solid state pyrolysis, as the required starting material [Os$_2$(CO)$_6$(μ-I)$_2$] was readily obtained from the reaction of Os$_3$(CO)$_{12}$ and I$_2$.[5]

These Os metal complexes were fully characterized *via* spectroscopic methods. Of particular interest is the IR ν(CO) spectrum of **1** in cyclohexane, which revealed three strong CO stretching bands at 2125, 2047 and 2031 cm^{-1} characteristic for the mutually orthogonal [Os(CO)$_3$] unit. The iodide complex **4** was then examined by a single crystal X-ray diffraction study. The result showed an asymmetric unit containing two crystallographically distinct, but structurally identical, molecules. As depicted in Fig. 1 the structure of one molecule reveals an octahedral Os metal arrangement, which is surrounded by a chelating dbm ligand, together with an iodide and three *facial* carbonyl ligands. The gross structure of **4** can be referred to those found in the closely related hexafluoroacetylacetonate derivative [Os(CO)$_3$(tfa)(hfac)][6] and the monometallic complexes such as [Os(CO)$_3$(tfa)$_2$] and [Os(CO)$_3$(pyS)$_2$],[7] pyS = pyridine-2-thionate, of which one potentially chelating organic ligand is converted to monodentate bonding mode in completing the six-coordinate geometry.

The absorption and luminescence spectra of representative complexes **1**, **2** and **4** are shown in Fig. 2, and the photophysical as well as electrochemical data are summarized in Table 1. Typically, these complexes exhibit the lowest energy absorption band in the visible region of *ca*. 367–380 nm with high absorptivity of $\varepsilon > 1.3 \times 10^4$ M^{-1}cm^{-1} at the peak maximum. Due to their spectral similarity with the absorption of the respective sodium salt (dbm)Na in acetonitrile solution (~ 352 nm), this absorption band can be reasonably assigned as an intraligand π–π^* transition of the deprotonated dbm. However,
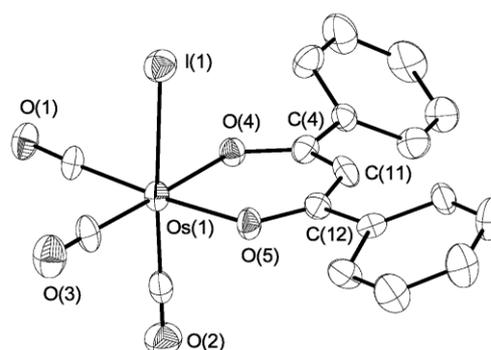
Fig. 1 The X-ray crystal structure of **4**; selected distances: Os(1)–C(1) = 1.917(7), Os(1)–C(2) = 1.928(8), Os(1)–C(3) = 1.896(7), Os(1)–O(4) = 2.088(4), Os(1)–O(5) = 2.085(4) and Os(1)–I(1) = 2.721(1) Å.‡

Table 1 Photophysical properties and electrochemical data of complexes **1**–**5**

Entry	Formula	λ_{abs}/nm, CH$_2$Cl$_2$ at RT (ε/M^{-1}cm^{-1})	λ_{em}/nm^a	τ_o/µs^a	Φ_{em}	k_r/10^3 s^{-1b}	E_{pa}/V^c	E_{pc}/V^c
1	[Os(CO)$_3$(tfa)(dbm)]	280 (21900) 367 (20000)	538 (541)^f	64 (3.0)^f	0.13	2.02	+1.75	−1.53
2	[Os(CO)$_3$Cl(dbm)]	285 (19100) 372 (16200)	557 (537)	46 (9.1)	0.13	2.76	+1.68	−1.60
3	[Os(CO)$_3$Br(dbm)]	278 (19200) 375 (15600)	563 (561)	29 (4.2)	0.08	2.82	+1.64	−1.58
4	[Os(CO)$_3$I(dbm)]	278 (23800) 380 (13500)	574 (602)	0.72, 38 (2.7)	0.007	0.18	+1.60	−1.59
5	[Os(CO)$_3$(SCN)(dbm)]	277 (26300) 372 (15300)	539 (545)	53 (3.4)	0.13	2.49	+1.74	−1.55
	[(dbm)Na]	352 (22100)^d	530^e	5 × 10^4	<10^{-3}	<0.05	—	−1.20

^{a} Solvent: CH$_2$Cl$_2$ and excitation wavelength: 380 nm. ^{b} k_r = Φ_{em}/τ. ^{c} In CH$_3$CN with 0.1 M ^{n}Bu$_4$NPF$_6$ (TBAH) supporting electrolyte and Ag/AgCl reference electrode at RT; scan rate 100 mV s^{-1}, while E_{pa} and E_{pc} refer to the irreversible anodic and cathodic peak potentials, respectively. ^{d} Data recorded in CH$_3$CN. ^{e} The emission data were taken in a 77 K methanol glass. ^{f} Data in parentheses () were obtained in the solid state. Note that a faster decay component (< 0.2 µs) was observed for **1**–**5** in the solid state possibly due to the defective sites. Its integrated intensity is <10% and is thus neglected.
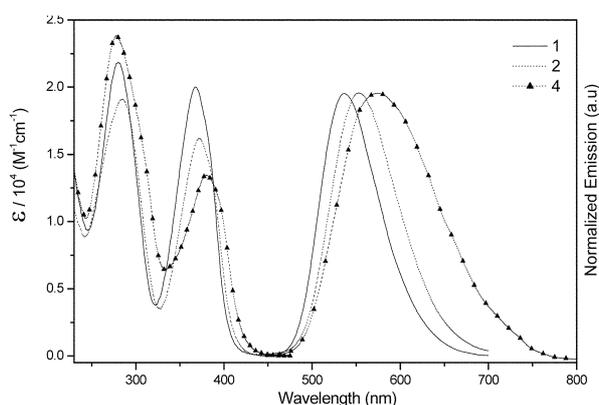
Fig. 2 Absorption and emission spectra of complexes **1**, **2** and **4** in CH$_2$Cl$_2$ solution.

because the corresponding ^{1}MLCT signal of the related Os(II) polypyridyl complexes also occurs in the same region,[8] the possibility of a small contribution from the MLCT transition cannot be ruled out.

Complexes **1**–**5** exhibit bright emission in deaerated CH$_2$Cl$_2$. The hypsochromic shift of the emission peak maximum is in the order of tfa ≈ SCN > Cl > Br > I, consistent with the trend of electron withdrawing strength destabilizing the HOMO of dbm and hence increasing the energy gap. The emission lifetime is unusually long (>20 µs),[9] while the quantum efficiencies, except for **4**, were measured to be as high as 0.08–0.13. In addition, the emission was drastically quenched by O$_2$ with a rate ~ 1.52 × 10^9 M^{-1}s^{-1} for **2** in CH$_2$Cl$_2$. These observations lead us to assign the emission to be phosphorescent in nature. Further support is given by the power-dependent relaxation dynamics. On increasing the excitation intensity the decay becomes non-single exponential, indicating the prevalence of triplet–triplet annihilation upon high triplet-state population. Note that a shorter lifetime was also observed for the iodide complex **4** (see Table 1), and is tentatively proposed to originate from photodissociation due to the weak Os–I bond, as indicated by the change of absorption spectral features as well as the decrease of 574 nm phosphorescence upon a long period of photolysis.

A comparative experiment was also performed for the dbm anion (dbm)Na in basified (NaOH) methanol, and a phosphorescence maximized at ~530 nm was resolved in a 77 K methanol glass, of which the spectral feature resembles that observed in complexes **1**–**5**. This result concludes that the room-temperature phosphorescence in **1**–**5** originates predominantly from the $^3\pi$–π^* manifold of ligated dbm. The main difference in phosphorescence properties lies in the much faster radiative decay rate in the Os complexes (see Table 1 for comparison),

manifesting the unusually strong spin–orbit coupling induced by Os.

A unique, strong phosphorescence was also observed for **1**–**5** in the solid state, and the corresponding emission and lifetime data are listed in Table 1. In comparison to that measured in the solution phase the lifetime in solid state is relatively short, possibly due to the crystal packing effect.

In summary, a new series of the Os(II) complexes with the dbm chelate were synthesized. The results represent a rare class of complexes possessing lowest excited states localized predominantly on the dbm ligand, resulting in unusually strong, long-lived phosphorescence in room-temperature fluid solution as well as in solid crystal. This class of Os(II) complexes with profound photophysical and electrochemical data provided may be advantageously exploited in a variety of photochemical studies such as OLED or photovoltaic devices. Furthermore, the current successes in assembling the Re-containing supramolecules may warrant a similar applicability of the dibenzoylmethanate Os(II) complexes. Work on the relevant subjects is in progress and will be published in a forthcoming full paper.

Notes and references

1 (a) D. J. Stufkens, *Comments Inorg. Chem.*, 1992, **13**, 359; (b) A. P. Zipp, L. Sacksteder, J. Streich, A. Cook, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, 1993, **32**, 5629; (c) L. Sacksteder, M. Lee, J. N. Demas and B. A. DeGraff, *J. Am. Chem. Soc.*, 1993, **115**, 8230; (d) B. D. Rossenaar, D. J. Stufkens and A. Vlcek, Jr., *Inorg. Chem.*, 1996, **35**, 2902; (e) V. W.-W. Yam, V. C.-Y. Lau and L.-X. Wu, *J. Chem. Soc., Dalton Trans.*, 1998, 1461; (f) A. Vogler and H. Kunkely, *Coord. Chem. Rev.*, 2000, **200–202**, 991; (g) D. R. Striplin and G. A. Crosby, *Coord. Chem. Rev.*, 2001, **211**, 163.

2 (a) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (b) S.-S. Sun and A. J. Lees, *Organometallics*, 2002, **21**, 39; (c) S. M. Woessner, J. B. Helms, J. F. Houlis and B. P. Sullivan, *Inorg. Chem.*, 1999, **38**, 4380; (d) V. W.-W. Yam, *Chem. Commun.*, 2001, 789.

3 A. J. Deeming, N. P. Randle, P. A. Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1988, 2753.

4 J.-H. Gong, D.-K. Hwang, C.-W. Tsay, Y. Chi, S.-M. Peng and G.-H. Lee, *Organometallics*, 1994, **13**, 1720.

5 S. Rosenberg, A. W. Herlinger, W. S. Mahoney and G. L. Geoffroy, *Inorg. Synth.*, 1989, **25**, 187.

6 H.-L. Yu, Y. Chi, C.-S. Liu, S.-M. Peng and G.-H. Lee, *Chem. Vap. Deposition*, 2001, **7**, 245.

7 A. J. Deeming, M. N. Meah, N. P. Randle and K. I. Hardcastle, *J. Chem. Soc., Dalton Trans*, 1989, 2211.

8 (a) J. V. Caspar, T. D. Westmoreland, G. H. Allen, P. G. Bradley, T. J. Meyer and W. H. Woodruff, *J. Am. Chem. Soc.*, 1984, **106**, 3492; (b) D. R. Striplin and G. A. Crosby, *Chem. Phys. Lett.*, 1994, **221**, 426; (c) M. E. Garcia Posse, N. E. Katz, L. M. Baraldo, D. D. Polonuer, C. G. Colombano and J. A. Olabe, *Inorg. Chem.*, 1995, **34**, 1830; (d) J. Y. K. Cheng, K.-K. Cheung and C.-M. Che, *Chem. Commun.*, 1997, 623.

9 Other examples are [MoCl$_{12}$]$^{2-}$, [Au(dppm)$_2$]$^{2+}$ and [Pt(dppe)(5,6-Me$_2$phen)]$^{2+}$, see: K. T. Wan and C. M. Che, *J. Chem. Soc., Chem. Commun.*, 1990, 140.