Heterododecanuclear Pt$_6$Ln$_6$ (Ln = Nd, Yb) arrays of 4-ethynyl-2,2′-bipyridine with sensitized near-IR lanthanide luminescence by Pt → Ln energy transfer†

Hai-Bing Xu, Li-Yi Zhang, Zai-Lai Xie, En Ma and Zhong-Ning Chen*

Received (in Cambridge, UK) 1st March 2007, Accepted 4th April 2007
First published as an Advance Article on the web 20th April 2007
DOI: 10.1039/b703135a

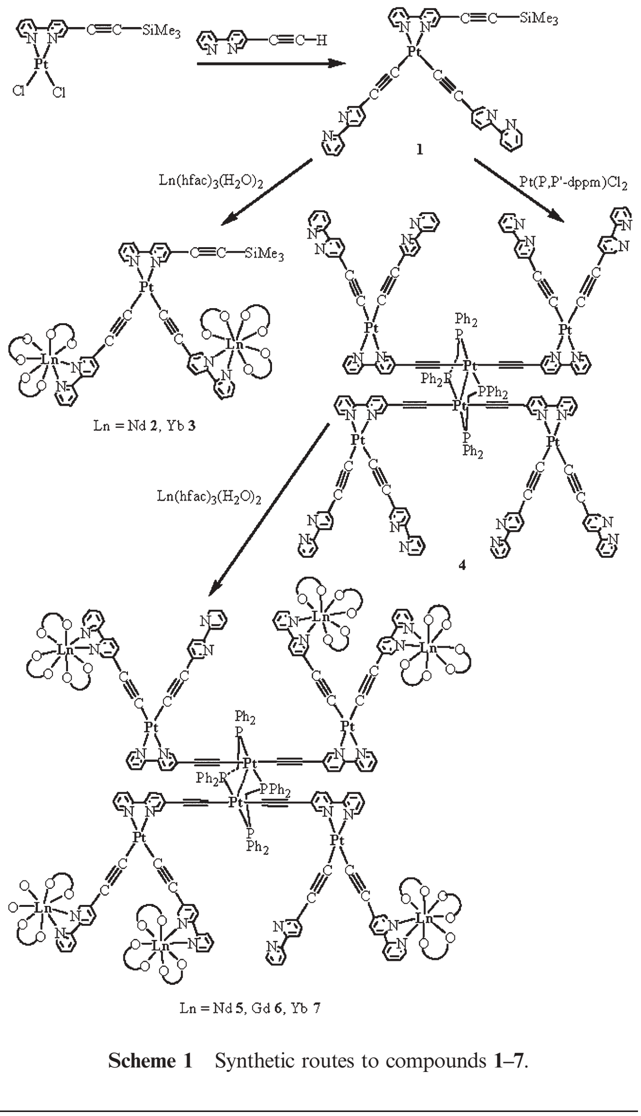
Heterododecanuclear Pt$_6$Ln$_6$ (Ln = Nd, Yb) complexes of 4-ethynyl-2,2′-bipyridine (HC≡Cbpy), prepared using emissive Pt(Me$_3$SiC≡Cbpy)(C≡Cbpy)$_2$ as an alkynyl bridging "ligand", afford sensitized near-infrared (NIR) lanthanide luminescence by Pt → Ln energy transfer from both Pt(bpy)(acetylide)$_2$ and Pt$_2$(dppm)$_2$(acetylide)$_2$ chromophores.

Near-infrared (NIR) luminescence of lanthanide complexes is currently attracting considerable interests in the fields such as light emitting diodes, optical communication, and biological assays *etc.*[1] Because of the low efficiency of f–f transitions, luminescence from lanthanides is usually sensitized by excitation of strongly absorbing organic ligands bound directly to the lanthanide centres through an antenna effect.[1] Alternately, a new approach for achieving NIR lanthanide emission has been established using d-block metal chromophores as sensitizers through efficient d → f energy transfer.[2] As transition metal chromophores can offer advantages such as intense charge transfer absorption in the visible region, facilitating intersystem crossing for a high triplet quantum yield, long-lived excited states, and facile detection of both quenching of the d-block chromophores and sensitised emission from the lanthanides, the approach with bimetallic d–f hybrid entity is highly appearing.[2–12]

Aiming at achieving NIR lanthanide luminescence through energy transfer from a d-block chromophore to lanthanide centre, a key step is to design suitable bifunctional bridging ligands with both "soft" donors (C, N or P) for the transition metal and "hard" donors (O or N) for the lanthanide centres. It is anticipated that bipyridyl-functionalized acetylides are excellent candidates as conjugated bridging ligands with acetylides and bipyridyl bound to the "soft" transition metal and "hard" lanthanide centres, respectively.[11,12] Reaction of PtCl$_2$(dppm-*P*,*P*′) with 5-ethynyl-2,2′-bipyridine or 5-ethynyl-1,10-phenanthroline gives diplatinum complexes Pt$_2$(μ-dppm)$_2$(C≡CR)$_4$ (R = 2,2′-bpy, 1,10-phen). Incorporation of the diplatinum species with Ln(hfac)$_3$ (Ln = Eu, Nd, Yb) through 2,2′-bpy or 1,10-phen chelating affords Pt$_2$Ln$_2$ or Pt$_2$Ln$_4$ arrays.[12] As anticipated, sensitisation of lanthanide emission by d(Pt$_2$) → π*(C≡C–R) ^{3}MMLCT (metal–metal to ligand charge transfer) excited state is successfully achieved through Pt → Ln energy transfer from the Pt^{II} alkynyl antenna chromophores.[12]

We describe herein the use of emissive complex **1** (Scheme 1) as a potential alkynyl "ligand" to react with PtCl$_2$(dppm-*P*,*P*′) for construction of hexanuclear Pt^{II} complex **4**, affording a series of Pt$_6$Ln$_6$ heterododecanuclear complexes by incorporation with Ln(hfac)$_3$ components through 2,2′-bipyridyl chelation.

As shown in Scheme 1, **1** was prepared by reaction of Pt(bpyC≡CSiMe$_3$)Cl$_2$ with HC≡Cbpy in the presence of CuI and Pr$^i{}_2$NH and purified by silica gel column chromatography.



Scheme 1 Synthetic routes to compounds **1–7**.

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China. E-mail: czn@fjirsm.ac.cn

† Electronic supplementary information (ESI) available: Detailed synthetic procedures and characterization for compounds **1–7**. See DOI: 10.1039/b703135a

Reaction of **1** with $PtCl_2(dppm\text{-}P,P')$ in the presence of KF and CuI gave hexanuclear Pt^{II} complex **4** as an orange product which is sparsely soluble in general organic solvents. Addition of 8.8 equiv. of $Ln(hfac)_3(H_2O)_2$ (Ln = Nd, Gd, Yb) to a suspension of **4** in dichloromethane induced formation of clear yellow solutions, from which Pt_6Ln_6 heterododecanuclear species were isolated as yellow crystals. In order to explore Pt → Ln energy transfer by different mediating pathways in Pt_6Ln_6 heterododecanuclear complexes, $PtLn_2$ (Ln = Nd **2**, Yb **3**) heterotrinuclear compounds were also prepared as model compounds for the subunits in Pt_6Ln_6 arrays.

1 and **7** were characterized by X-ray crystallography.‡ The Pt_6Yb_6 array in **7** (Fig. 1) consists of $Pt_6(\mu\text{-dppm})_2(C{\equiv}Cbpy)_{12}$ incorporating with six $Ln(hfac)_3$ components through 2,2′-bipyridyl chelating. It is centrosymmetric with inversion centre at the midpoint between Pt1 and Pt1A atoms. Formation of the Pt_6Yb_6 complex instead of the designed Pt_6Yb_8 array originates probably from steric effects as well as flexibility of 2,2′-bipyridyl bonding. The $Pt_6(\mu\text{-dppm})_2(C{\equiv}Cbpy)_{12}$ moiety is made up of $Pt_2(\mu\text{-dppm})_2(C{\equiv}Cbpy)_4$ incorporating with four $Pt(C{\equiv}Cbpy)_2$ units *via* 2,2′-bipyridyl chelating in the diplatinum unit. The $Pt_2(\mu\text{-dppm})_2(C{\equiv}Cbpy)_4$ framework displays a face-to-face conformation with the bpy···bpy distance being 3.42 Å, suggesting that a π–π stacking is operative between face-to-face bipyridyl rings.[13] The Pt1–Pt1A distance is 3.2212(6) Å, comparable to those found in other complexes with $Pt_2(\mu\text{-dppm})_2(C{\equiv}CR)_4$ moieties[12,13] and suggesting the presence of moderate Pt–Pt contact. The C≡C–Pt–C≡C arrays in $Pt_2(\mu\text{-dppm})_2(C{\equiv}Cbpy)_4$ unit are *trans*-oriented and deviate slightly from linearity with the angles C≡C–Pt and C–Pt–C being 171.8(7)–179.2(9)° and 175.2(3)°, respectively. In contrast, the bpyC≡C–Pt–C≡Cbpy arrays in four $Pt(bpy)(acetylide)_2$ moieties are *cis*-arranged.

As observed in **1**, the four $Pt(bpy)(acetylide)_2$ moieties in $Pt_6(\mu\text{-dppm})_2(bpyC{\equiv}C)_{12}$ assembly are characteristic of Pt^{II} square-planar geometries built by 2,2′-bipyridyl chelating and bis(acetylide) σ-coordination. Of the eight bpyC≡C ligands in the four $Pt(bpy)(acetylide)_2$ moieties, six are bound to $Yb(hfac)_3$ units through 2,2′-bipyridyl chelating whereas the other two are not coordinated. Compared with that in **1** (19.7°), the dihedral angle between the two C≡Cbpy planes in the $Pt(bpy)(C{\equiv}Cbpy)_2$ moiety is enhanced significantly (32.5 and 50.5°) after incorporating with $Yb(hfac)_3$ units. The Yb^{III} centres are eight-coordinated with N_2O_6 donors to form distorted square antiprisms. The Pt···Pt distances through bridging C≡Cbpy are 8.54 and 8.52 Å for Pt1···Pt2 and Pt1···Pt3, respectively. The Pt···Yb separations across bridging C≡Cbpy are 8.41, 8.80 and 8.63 Å for Pt2···Yb1, Pt3–Yb2 and Pt3–Yb3, respectively. The Pt1···Yb1, Pt1···Yb2 and Pt1···Yb3 distances are 16.73, 10.48 and 16.37 Å, respectively.

The UV-vis absorption spectrum of **1** in dichloromethane exhibits high-energy bands at 229 and 324 nm due to dppm-centred and π→π* (bpyC≡C) transitions, respectively. A broad low-energy band at 416 nm originates likely from d(Pt) → π*(bpy) MLCT (metal to ligand charge transfer) transitions.[14] Upon formation of $Pt^{II}Ln^{III}{}_2$ heterotrinuclear arrays (Ln = Nd **2**, Yb **3**), the low-energy MLCT absorption shows an obvious blue shift to higher energy.[11]

For hexanuclear Pt^{II} complex **4**, the low-energy absorption with maximum at 382 nm tailing to 500 nm is probably a composite band, originating from both d(Pt) → π*(bpy) MLCT transition in $Pt(bpy)(acetylide)_2$ the chromophore[14] and $d(Pt_2)$ → π*(C≡Cbpy) MLCT transition in the $Pt_2(dppm)_2(acetylide)_2$ moiety.[12,13] On formation of the Pt_6Ln_6 arrays, the low-energy band shows an obvious hypsochromic shift (Fig. S2, ESI†) relative to that of the precursor complex **4**. By addition of portions of $Yb(hfac)_3(H_2O)_2$ to a dichloromethane solution of **4**, the low-energy band shifts from 382 to *ca.* 370 nm (Fig. S3, ESI†), which is likely responsible for the colour weakening during the reaction.

1 exhibits intense emission in both the solid state and degassed solution with sub-microsecond lifetime (Table 1) at ambient temperature, arising most likely from d(Pt) → π*(bpy) ^{3}MLCT transitions.[14] With $\lambda_{ex} > 400$ nm, **4** emits luminescence with the maximum at 566 cm^{-1} and lifetime of 0.73 μs in degassed dichloromethane at 298 K. Because of the presence of two types of Pt-based chromophore, emission of **4** is likely caused by both d(Pt) → π*(bpy) ^{3}MLCT transition[14] and $d(Pt_2)$ → π*(C≡Cbpy) ^{3}MMLCT transition[12,13] in view of the short intramolecular Pt–Pt (3.2212(6) Å) contacts in the solid state.

Upon irradiation with $\lambda_{ex} > 360$ nm, $PtLn_2$ or Pt_6Ln_6 complexes exhibit emissions characteristic of the corresponding lanthanide ions with lifetimes on the microsecond ranges (Table 1) in both the solid state and in dichloromethane at 298 K. Even with excitation of the tail of the Pt-based MLCT absorption at 450 nm, characteristic NIR emissions from lanthanide centres are still observed, revealing unambiguously sensitization of lanthanide

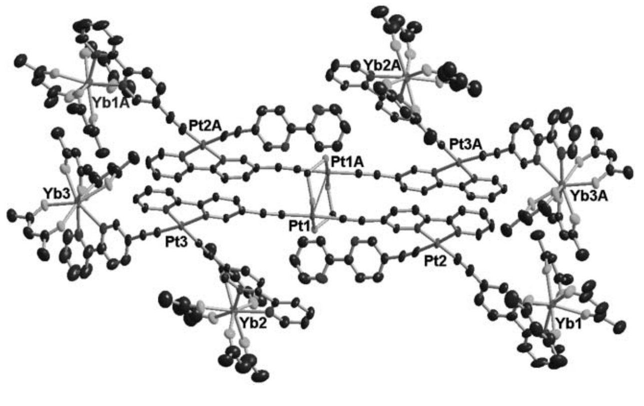


Fig. 1 ORTEP drawing of **7** showing 30% thermal ellipsoid. The F atoms and phenyl rings are omitted for clarity. A: 1 − *x*, 1 − *y*, 1 − *z*.

Table 1 Luminescent data for compounds **1–7** at 298 K

Compound	Solid λ_{em}/nm (τ/μs)[a]	CH_2Cl_2 λ_{em}/nm (τ/μs)[a]	$10^3\Phi_{em}$
1	640 (0.20)	575 (0.30)	104[b]
2	1061 (weak)	1061 (weak)	
3	980 (15.1)	980 (11.8)	5.9[c]
4	648 (weak)	566 (0.73), 608sh	3.0[b]
5	1061 (weak)	1060 (weak)	
6	593 (0.502)	563 (0.84)	0.7[b]
7	980 (13.2)	980 (12.1)	6.1[c]

[a] The excitation wavelength in the lifetime measurement is 397 nm. [b] The emission quantum yields of **1**, **4** and **6** were measured in degassed dichloromethane solutions at 298 K and estimated relative to $[Ru(bpy)_3](PF_6)_2$ in acetonitrile as the standard ($\Phi_{em} = 0.062$). [c] The quantum yield of Yb complexes in CH_2Cl_2 solutions is estimated by the equation $\Phi_{Ln} = \tau_{obs}/\tau_0$, in which τ_{obs} is the observed emission lifetime and τ_0 is the radiative or 'natural' lifetime with τ_0 = 2 ms for Yb^{III}.[4,5]

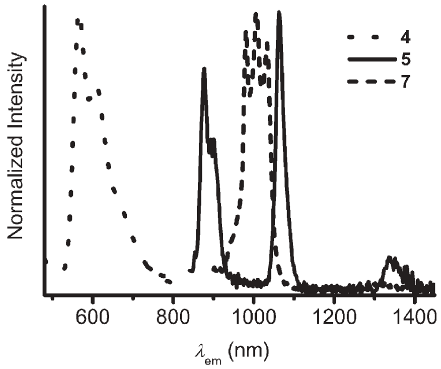


Fig. 2 Emission spectra of **4** (dotted line), **5** (solid line) and **7** (dashed line) in dichloromethane at 298 K.

luminescence is indeed achieved by energy transfer from Pt-based antenna triplet states. As expected (Fig. 2), three emission bands occur for Pt^{II}–Nd^{III} complexes at *ca.* 865, 1060 and 1330 nm ($^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$), and one for Pt^{II}–Yb^{III} complexes at *ca.* 980 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$).

For $PtLn_2$ (Ln = Nd **2**, Yb **3**) heterotrinuclear species, the Pt^{II} chromophore-based ^{3}MLCT emission in the visible region disappeared entirely, indicating unambiguously that the $Pt^{II}(bpy)(C{\equiv}C)_2$-based emission is entirely quenched because of rapid and complete energy transfer from the Pt^{II}-based energy donors. Titration of **1** with $Yb(hfac)_3(H_2O)_2$ in dichloromethane induced rapid attenuation of the Pt-based emission so as to give complete quenching of the luminescence when 2 equiv. of $Yb(hfac)_3(H_2O)_2$ was added (Fig. S4, ESI†).

In contrast, residual emissions due to Pt_6 alkynyl moiety are observed with maxima at 520–650 nm for Pt_6Ln_6 (Ln = Nd **5**, Yb **7**) compounds, revealing incomplete energy transfer from the Pt^{II}-based antenna donors to the Ln^{III} centres in **5** and **7**. As there exist both $Pt(bpy)(acetylide)_2$ and $Pt_2(dppm)_2(acetylide)_2$ antenna chromophores in the Pt_6Ln_6 species, sensitized NIR lanthanide luminescence in **5** (Ln = Nd) and **7** (Ln = Yb) is likely induced by Pt → Ln energy transfer from both d(Pt) → π*(bpy) ^{3}MLCT and d(Pt_2) → π*(C≡Cbpy) ^{3}MMLCT triplet states. As revealed in $PtLn_2$ (Ln = Nd **2**, Yb **3**) model compounds, Pt → Ln energy transfer from the $Pt(bpy)(acetylide)_2$ antenna group to the lanthanide centre is rapid and complete, due to probably the direct linkage of $Pt(bpy)(C{\equiv}CR)_2$ chromophores with lanthanide centres, the short Pt···Ln distances (8.4–8.80 Å) as well as the favourable conjugation in the bridging ligand C≡Cbpy. By contrast, Pt → Ln energy transfer from the $Pt_2(dppm)_2$-$(acetylide)_2$ cluster chromophore is indirect, long-range (Pt···Ln = 10.5, 16.4 and 16.7 Å) and incomplete, inducing some residual Pt^{II}-based emission in the Pt_6Ln_6 species.

The lifetimes of residual Pt-based emissions are 16 ns for Pt_6Nd_6 (**5**) and 430 ns for Pt_6Yb_6 (**7**) species in dichloromethane at ambient temperature. Taking into account the statistical factor,[6c] the rates k_{ET} of Pt → Ln energy-transfer from antenna group $Pt_2(dppm)_2(acetylide)_2$ can thus be estimated by the equation $k_{ET} = (\tau^{-1} - \tau_0^{-1})/6$,[2,4,6c,11] where τ is the lifetime of residual Pt-based emission in Pt_6Ln_6 (Ln = Nd **5**, Yb **7**) species, and τ_0 (840 ns) is the "unquenched" lifetime in the reference Ln_6Gd_6 (**6**) complex without d → f energy transfer. The calculated k_{ET} are 1.02×10^7 s^{-1} for Pt_6Nd_6 (**5**) and 1.83×10^5 s^{-1} for Pt_6Yb_6 (**7**) species. The faster Pt → Ln energy transfer for the Pt_6Nd_6 complex than that for Pt_6Yb_6 species can be rationalized by the better spectroscopic overlap between the emission spectrum of the Pt^{II}-based antenna chromophore and the absorption spectrum of the Nd^{III} ion.[2,11]

In summary, a feasible synthetic route is established for preparation of a series of Pt_6Ln_6 arrays using emissive $Pt(Me_3SiC{\equiv}Cbpy)(C{\equiv}Cbpy)_2$ as an alkynyl bridging "ligand". Sensitized NIR lanthanide luminescence is successfully attained by Pt → Ln energy transfer from both d(Pt) → π*(bpy) ^{3}MLCT and d(Pt_2) → π*(C≡Cbpy) ^{3}MMLCT triplet states.

We acknowledge financial supports from the NSFC (90401005, 20490210, 20521101, and 20625101), NSF of Fujian Province (E0310029) and the Key Project from CAS (KJCX2-YW-H01).

Notes and references

‡ *Crystal data* for **1**: $C_{39}H_{30}N_6PtSi$, M_r = 805.87, monoclinic, space group $P2_1/c$, a = 7.213(5), b = 18.508(12), c = 24.891(16) Å, β = 94.735(9)°, V = 3311(4) $Å^3$, Z = 4, D_c = 1.616 g cm^{-3}, μ(Mo-Kα) = 4.312 mm^{-1}, T = 293(2) K, 2θ = 55°, $R1$ = 0.0747, $wR2$ = 0.1502 for 4672 reflections with $I > 2\sigma(I)$, GOF = 1.075.

Crystal data for $\mathbf{7}\cdot 2C_6H_{14}\cdot 9CH_2Cl_2\cdot 7H_2O$: $C_{305}H_{206}Cl_{18}F_{108}N_{24}O_{43}P_4Pt_6Yb_6$, M_r = 9917.70, triclinic, space group $P\bar{1}$, a = 19.5811(3), b = 21.8700(1), c = 22.8393(4) Å, α = 72.372(3), β = 87.759(4), γ = 77.873(4)°, V = 9110.2(2) $Å^3$, Z = 1, D_c = 1.808 g cm^{-3}, μ(Mo-Kα) = 4.087 mm^{-1}, T = 133 K, 2θ = 50°, $R1$ = 0.0558, $wR2$ = 0.1392 for 25786 reflections with $I > 2\sigma(I)$, GOF = 1.078.

CCDC 634044 and 634045. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703135a

1 J.-C. G. Bunzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048.
2 S. I. Klink, H. Keizer and F. C. J. M. van Veggle, *Angew. Chem., Int. Ed.*, 2000, **39**, 4319.
3 P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat and L. De Cola, *Angew. Chem., Int. Ed.*, 2005, **44**, 1806.
4 N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner and M. D. Ward, *Chem. Commun.*, 2003, 1134; N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner and M. D. Ward, *Chem.–Eur. J.*, 2003, **9**, 5283.
5 S. J. A. Pope, B. J. Coe, S. Faulkner, E. V. Bichenkova, X. Yu and K. T. J. Douglas, *J. Am. Chem. Soc.*, 2004, **126**, 9490; S. J. A. Pope, B. J. Coe and S. Faulkner, *Chem. Commun.*, 2004, 1550.
6 D. Imbert, M. Cantuel, J.-C. G. Bünzli, G. Bernardinelli and C. Piguet, *J. Am. Chem. Soc.*, 2003, **125**, 15698; S. Torelli, D. Imbert, M. Cantuel, G. Bernardinelli, S. Delahaye, A. Hauser, J.-C. G. Bünzli and C. Piguet, *Chem.–Eur. J.*, 2005, **11**, 3228; M. Cantuel, F. Gumy, J. C. G. Bunzli and C. Piguet, *Dalton Trans.*, 2006, 2647.
7 A. Beeby, R. S. Dickins, S. FitzGerald, L. J. Govenlock, C. L. Maupin, D. Parker, J. P. Riehl, G. Siligardi and J. A. G. Williams, *Chem. Commun.*, 2000, 1183.
8 P. B. Glover, P. R. Ashton, L. J. Childs, A. Rodger, M. Kercher, R. M. Williams, L. De Cola and Z. Pikramenou, *J. Am. Chem. Soc.*, 2003, **125**, 9918.
9 P. D. Beer, F. Szemes, P. Passaniti and M. Maestri, *Inorg. Chem.*, 2004, **43**, 3965.
10 D. Guo, C.-Y. Duan, F. Lu, Y. Hasegawa, Q.-J. Meng and S. Yanagida, *Chem. Commun.*, 2004, 1486.
11 T. K. Ronson, T. Lazarides, H. Adams, S. J. A. Pope, D. Sykes, S. Faulkner, S. J. Coles, M. B. Hursthouse, W. Clegg, R. W. Harrington and M. D. Ward, *Chem.–Eur. J.*, 2006, **12**, 9299.
12 H.-B. Xu, L.-X. Shi, E. Ma, L.-Y. Zhang, Q.-H. Wei and Z.-N. Chen, *Chem. Commun.*, 2006, 1601.
13 C.-K. Hui, B. W.-K. Chu, N. Zhu and V. W.-W. Yam, *Inorg. Chem.*, 2002, **41**, 6178.
14 S.-C. Chan, M. C. W. Chan, Y. Wang, C.-M. Che, K.-K. Cheung and N. Zhu, *Chem.–Eur. J.*, 2001, **7**, 4180.