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Strong optical limiting capability of a triosmium cluster bonded indium porphyrin complex [(TPP)$InOs_3(\mu\text{-}H)_2(CO)_9(\mu\text{-}\eta^2\text{-}C_5H_4N)$]

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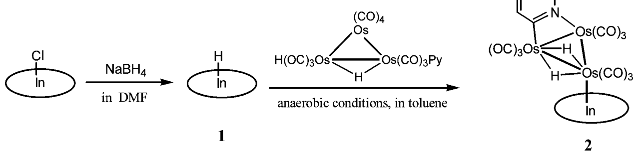
The metal–metal bonded indium porphyrin–osmium cluster complex [(TPP)$InOs_3(\mu\text{-}H)_2(CO)_9(\mu\text{-}\eta^2\text{-}C_5H_4N)$] was first synthesized and characterized using the indium porphyrin hydride as the precursor. The complex has very good optical limiting performance with determined optical limiting threshold of 0.4 J cm^{-2}.

Remarkable development has recently been made in the design of metal porphyrin derivatives incorporating metal centers as components for light harvesting models,[1] molecular-scale devices,[2] conjugated porphyrin polymers,[3] and supramolecular systems.[4] In most of the model compounds studied so far, the metal center(s) are linked at the peripheral positions (*meso* or *β* positions) of the porphyrin ring. Thus the electronic interaction between the two moieties in the supramolecular assembly has not been effectively explored. In order to increase the electronic interaction between the two chromophores and therefore dictate the properties of the final arrangement, here we designed and synthesized the new model compound with metal–metal bond between metal porphyrin and osmium carbonyl cluster using the metal porphyrin hydride as the precursor.

The precursor indium porphyrin hydride [In(TPP)H] (TPP = 5,10,15,20-tetraphenylporphrnato) (**1**) was synthesized by the similar route as its gallium analogue by reducing porphyrin chloride with sodium borohydride in *N*,*N*-dimethylformamide.[5] Treatment of equimolar ratio of **1** with $H(\mu\text{-}H)Os_3(CO)_{10}(C_5H_5N)$ in toluene at 80 °C for 1 h under anaerobic conditions affords after purification by preparative TLC (SiO_2, toluene : hexane, 1 : 2) the metal cluster bonded porphyrin compound [(TPP)$InOs_3(\mu\text{-}H)_2(CO)_9(\mu\text{-}\eta^2\text{-}C_5H_4N)$] (**2**) in 56% ($R_f$ = 0.43) yield as the major product (Scheme 1).†

Dark green single crystals of **2** suitable for X-ray crystallographic analysis were obtained by slow solvent diffusion of ethyl ether into a toluene solution at −20 °C.‡ Fig. 1 shows the molecular structure of **2** that has a Os_3 cluster over the TPP ring with the Os(1)–In distance of 2.7142(8) Å. The geometry of the indium porphyrin is not greatly influenced by the attachment of the osmium cluster. The indium atom is located 0.811 Å above the mean porphyrin plane, which is larger than the values 0.463–0.791 Å for the reported indium porphyrin complexes.[6] The metal porphyrin moiety can be looked as a one-electron donor and located at the equatorial position of the Os_3 plane. The pyridine ring is ortho-metallated and bridges one edge of the Os_3 triangle adopting a $\mu\text{-}\eta^2$ coordination mode and is almost perpendicular to the Os_3 plane with the dihedral angle of 84.7°. The pyridine ring bridged Os(2)–Os(3) edge (2.7816(9) Å) is significant shorter than the other two unbridged edges (averaged 3.0604(9) Å), which is contrary to the observations of the reported *N*-heterocyclic ligands coordinated Os_3 cluster derivatives adopting the $\mu\text{-}\eta^2$-mode *via* a σ Os–C and Os–N bond where bridged edges are usually longer than the unbridged ones.[7] Although the hydrides are not crystallographically located, we can tentatively assign the two spectroscopically detected hydrides to be bridging across the Os(1)–Os(2) edge on the basis of the electron count of 17 each for the Os(1) and Os(2) unit. The unusual orientation of equatorial CO groups gives further support for the assignment. The Os(1)–Os(2) edge is associated with a much large CO_{eq}–Os–Os angle than the other two edges (∠C(222)–Os(2)–Os(1) = 114.8(2)°, ∠C(223)–Os(2)–Os(3) = 87.0(2)°, ∠C(112)–Os(1)–Os(3) = 110.4(2)°, ∠C(333)–Os(3)–Os(2) = 97.5(2)°, ∠C(332)–Os(3)–Os(1) = 104.6(2)°).



Scheme 1

Compared with the electronic absorption spectra of [In(TPP)Cl] and **1**, the Soret and Q bands of **2** are clearly perturbed and remarkably shifted (see Fig. 2). Like the UV-vis spectra for the series of (Por)In-ML where Por is a dianion of the porphyrin ligand and ML is a metal carbonyl moiety,[8] the Soret band of **2** splits into two bands (labeled band I and II). The band II (located at 452 nm) involves a π→π* electronic transition and shows a red shift of 15 nm and 27 nm when the axial ligand H in **1** or Cl in [In(TPP)Cl] is replaced with Os_3 moiety in **2**. The extra absorption in 384 nm (band I) is a charge-transfer band from the indium atom to the porphyrin ring, $a_{2u}(5P_z) \rightarrow e_g(\pi^*)$, to which a significant contribution of the charge transfer from the metal–metal bond is expected. The higher electron donating ability of Os_3 moiety in **2** is also

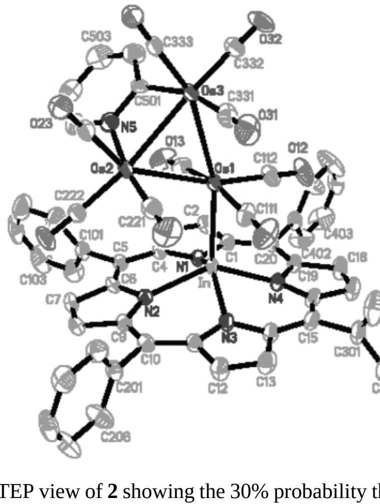


Fig. 1 ORTEP view of **2** showing the 30% probability thermal ellipsoids (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: In–N(1) 2.217(5), In–N(2) 2.192(5), In–N(3) 2.200(5), In–N(4) 2.205(5), In–Os(1) 2.7142(8), Os(1)–Os(2) 3.0479(8), Os(1)–Os(3) 3.0730(9), Os(2)–Os(3) 2.7816(9), Os(2)–N(5) 2.116(6), Os(3)–C(501) 2.123(7); In–Os(1)–Os(2) 108.98(3), In–Os(1)–Os(3) 163.03(2), Os(1)–Os(2)–Os(3) 63.43(3), Os(2)–Os(3)–Os(1) 62.51(2), Os(3)–Os(1)–Os(2) 54.06(2).

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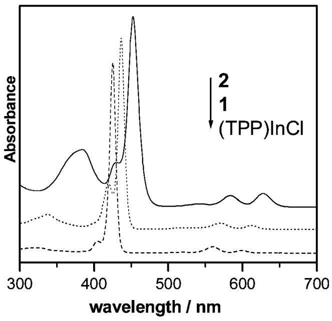

Fig. 2 UV-vis spectra of compounds **2** (solid line), **1** (dotted line) and In(TPP)Cl] (dashed line).

demonstrated by the relatively low value of the ratio of molar absorption between band II and I ($\varepsilon_{II}/\varepsilon_I$ = 3.3). This is consistent with the observation that the carbonyl groups vibrational absorption in **2** appear in a higher wavenumber region. It is obvious that the direct and strong electronic interaction between the porphyrin and osmium cluster moieties is achieved in the axially metal–metal bonded configuration of **2**.

Compound **2** has a relatively low linear absorption in the wavelength region above 460 nm. We also observed that **2** possesses large optical limiting (OL) effects. The measurement of the transmitted pulse energy was conducted with a full collection of the transmitted pulse, and no aperture was used. The OL capability utilizing only the NLO absorption is demonstrated in Fig. 3. The light energy transmitted starts to deviate from Beer's law as the input light fluence reaches *ca.* 0.04 J cm^{-2}, and the solution becomes less transparent as the incident fluence rises. The limiting threshold (fluence at which transmittance drops to half its linear value) of **2** is 0.4 J cm^{-2} in toluene solution when irradiated by 20 Hz repetition-rate laser pulse. This value is four times better than that of C_{60}, which is considered as one of the best optical limiting materials.[9] This larger OL capability of compound **2** should make it a very promising candidate for broad-band OL application.

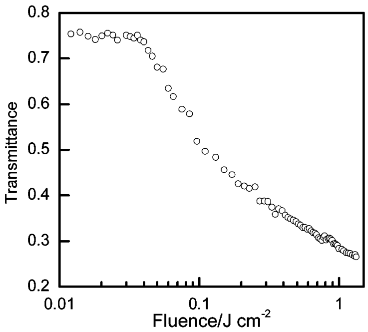

Fig. 3 Optical limiting response of a toluene solution of **2** obtained for 5 ns, 532 nm laser pulses with 20 Hz pulse interval. The solution was loaded in a 1 mm cell with a linear transmittance of 75%.

Notes and references

† Selected spectroscopic data for **2**: ^{1}H NMR (C_6D_6, 500 MHz) δ: 9.17 (s, 8H, pyrrole-H), 8.64 (m, 4H, o-H), 8.08 (m, 4H, o-H), 7.48 (m, 12H, m,p-H), 7.13 (m, 4H, pyridine-H), −15.37 (s, 1H, M–H), −19.5 (s, 1H, M–H); FAB *m/z* 1628 (M$^+$); IR (hexane) ν_{CO}/cm^{-1}: 2105 (w), 2085 (m), 2064 (s), 2053 (s), 2046 (s), 2024 (s), 2011 (s), 2004 (vs), 1997 (m), 1977 (w), 1969 (w); UV-vis [λ_{max} (toluene)/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})]: 627(6), 583(5), 541(1), 452(78), 429(18), 384(24)

‡ Crystal data for **2**: $C_{58}H_{32}InN_5O_9Os_3\cdot\frac{1}{2}C_7H_8$, M = 1674.38, triclinic, a = 12.210(2), b = 13.470(3), c = 18.740(4) Å, α = 95.22(3), β = 99.08(3), γ = 95.24(3)°, V = 3013(1) Å^3, T = 293(2) K, space group $P1$, Z = 2, μ(Mo–K$_\alpha$) = 6.737 mm^{-1}, GOF = 1.017, R_1 = 0.0395 [$I > 2\sigma(I)$], 19302 reflections measured, 13496 unique (R_{int} = 0.0331) which were used in all calculations. The final $wR(F^2)$ was 0.1048 (all data). CCDC 209027. See http://www.rsc.org/suppdata/cc/b3/b304349e/ for crystallographic data in .cif or other electronic format.

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