

## Increased Luminescent Lifetimes of Ru(II) Complexes

Photovoltaic systems for solar light harvesting offer a potential route to low power electricity. Ruthenium (Ru) complexes with a bpy (2,2'-bipyridine) ligand have traditionally been used in this research and in Grätzel cells, as they have excellent photophysical properties. Ru(tpy)<sub>2</sub><sup>2+</sup> (2,2':6',2''-terpyridine) is a chromophore that has been used in multinuclear structures, but its room temperature excited-state lifetime is < 250 ps. Longer lifetimes have been obtained for Ru(II) terpyridine complexes where one tpy ligand is attached to a coplanar pyrimidine while the other tpy moiety has a 9-anthryl organic chromophore. The longer lifetimes are due to a bichromophoric effect (the triplet states of the metal-to-ligand charge-transfer (<sup>3</sup>MLCT) and of the anthracene are in equilibrium). In this case the Ru and anthryl chromophores are on the same ligand and synthesis is not easy.

Now, researchers from the Université de Montréal, Canada, and Università di Messina, Italy, have synthesised a new series of luminescent Ru(tpy)<sub>2</sub><sup>2+</sup> species where the chromophores are separated by > 1 nm. The 9-anthryl chromophore

(the energy reservoir) is in the tpy moiety not involved in the <sup>3</sup>MLCT emitting level, while the 2-pyrimidyl-tpy subunit is involved in extended electron delocalisation.

In their method, the 9-anthryl chromophore is inserted into the 4'-position of the tpy moiety, giving a 4'-(9-anthryl)-2,2':6',2''-tpy Ru(II) complex. This started bichromophoric behaviour by lowering the <sup>3</sup>MLCT state of Ru(tpy)<sub>2</sub><sup>2+</sup> via the 2-pyrimidyl-tpy subunit, and increased the luminescence lifetimes because of the excited-state equilibrium. The luminescence lifetimes are long compared to those for Ru(tpy)<sub>2</sub><sup>2+</sup>.

This method gives separated chromophores on different ligands with long-lived excited states. It may allow special design of the Ru tpy moiety and the organic chromophore, and could result in compounds with specific photophysical properties.

### References

- 1 M. Grätzel, *Platinum Metals Rev.*, 1994, 38, (4), 151
- 2 J. Wang, G. S. Hanan, F. Loiseau and S. Campagna, *Chem. Commun.*, 2004, (18), 2068

## Carbon Nanotube Particulates in Electron Emitters

Scientists at Carbon Nanotechnologies, Inc., Houston, Texas, U.S.A., have produced carbon (C) nanotubes with one or more walls and outer wall diameters 0.5 to 3 nm (*World Patent* 2004/048,263). Using a gaseous C-containing feedstock, preferably, methane, but other hydrocarbons, alcohols and/or CO are permitted, they contacted a catalyst of Fe, Mo, Ru, Rh, Pd, Os, Ir or Pt, on a particulate support (magnesia of cross-section < 1000 μm) at 500–1500°C. The C nanotube particulates produced were then annealed and the support material was removed. The resulting particulates (enmeshed C nanotubes of ropes of cross-section 10–50 nm) retained the support's approximate shape and size.

The C nanotubes can be activated by etching, and were blended with a matrix material of thermoplastic or thermoset polymer, metal or ceramic. The C nanotube particulates could be well dispersed in the polymers and had high conductivity at low loadings.

Such pastes of polymers and C nanotubes find use in a range of electron emission devices. For example, entangled C nanotubes with one or more walls can be used to produce cathode components in field emission devices, such as electron discharge tubes, amplifiers, and oscillators. As electrical emitters, the C nanotube particulates exhibit a low 'turn on' emission field. DOI: 10.1595/147106704X15149

## Palladium-Iron Dispersed in Carbon

Fine metal or alloy particles dispersed in carbon (C) can be used in catalysis or in magnetic materials. Metal is dispersed in C either by the pyrolysis of organometallics or by reduction of metal chlorides intercalated in graphite. However the method of placing alloys in C by intercalation has not yet been successfully achieved.

Now, scientists in Japan (1) have developed a method to disperse fine particles of Pd-Fe alloy in a C matrix. This was achieved first by reduction of PdCl<sub>2</sub> with natural graphite flake. After heat and other treat-

ments coin-shaped Pd metal particles of ~ 50 nm were formed within the carbon layers.

FeCl<sub>3</sub> was then intercalated using the conventional two-bulb method. Reduction resulted in Pd and Fe coexisting within the graphite. To create an alloy the sample was further heat treated in high purity argon. XRD indicated lines of crystallised Pd-Fe alloy. This alloy was found to contain 6 wt.% Pd and 15 wt.% Fe.

### Reference

- 1 H. Shioyama and X. Min, *Carbon*, 2004, 42, (10), 2127