Technology around photoluminescent compounds

A research group led by Dr Violeta Sicilia of the University of Zaragoza, Spain, presents the technological applications for photoluminescent compounds in SSL and chemosensing

The area of platinum chemistry and their compounds' enthralling photoluminescent properties has grown over recent decades into an extremely productive and multidisciplinary research field for practical applications in medicine, electronics, biomaterials, sensing and lighting. For ten years now we have had a longstanding interest in developing new high-tech materials based on the photoluminescent compounds of platinum(II), containing cyclometalated groups such as imines or N-heterocyclic carbenes and combined with different ancillary ligands. The luminescent colour of these compounds can be tuned by changing the nature of both the cyclometalated and the ancillary ligands, and also by controlling the existence of Pt···Pt interactions. Therefore, we have been able to prepare a range of products that have resulted in efficient blue, green-yellow, yellow-orange and orange-red emitters. It has been proved that some of them have a great technological potential as:

1) Phosphor converter in LEDs for solid state lighting: We have prepared new stable and efficient yellow-emitting compounds that also absorb photons in the UV-blue spectral range (See Fig. 1a). Among them, compound [Pt(C^C*)(acac)] (C^C* = cyclometalated N-heterocyclic carbene; acac= acetylacetone) was used as a phosphor converter in an integrated white LED package (See Fig. 1b). The phosphor powder was homogeneously suspended in the encapsulating silicone and the mixture used to coat a commercial blue LED, which was used as pumping source. The phosphor absorbs some of the blue light from the LED and then re-emits it down-converted into longer wavelengths. White light is perceived when the unabsorbed blue light from the LED is mixed with the yellow light emitted from the phosphor (See Figs. 1a, 1c. Sicilia, V *et al. Chem. Eur. J.* 2015, 21, 1620-1631).

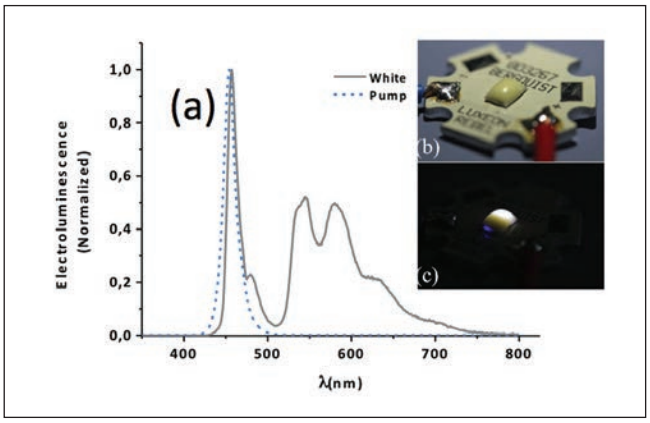

Fig. 1

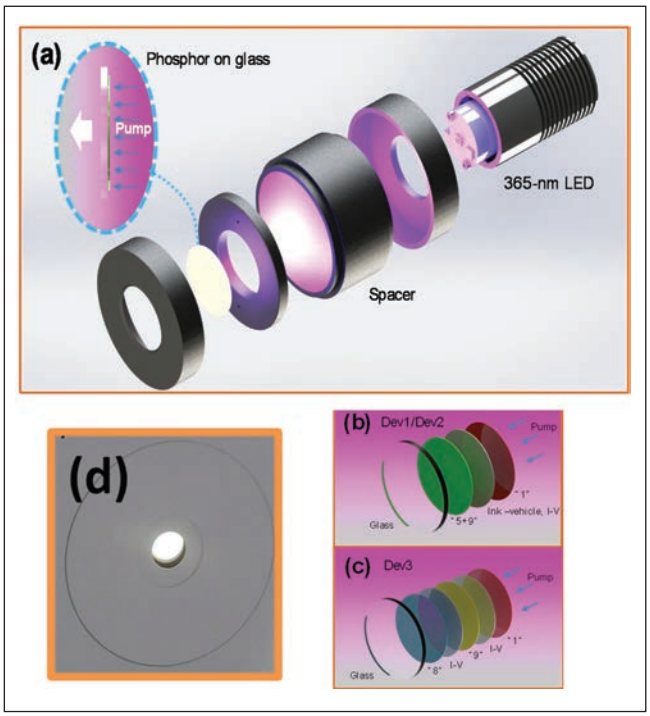

Fig. 2

2) Basic phosphor components of remote-phosphor white light emitting devices: We have prepared new stable and efficient blue and yellow-emitting compounds with quantum yields of up to 95%, able to be used in white light-emitting devices using UV LED as pumping source. Compounds $[Pt(R\text{-}C\hat{}C^*)(CNR')_2]PF_6$ (R-C^C* = cyclometalated N-heterocyclic carbene, CNR'= isocyanide) give rise to a variety of emission colours depending on the R and R' substituents. The most efficient blue and yellow emitters, combined with the red one [Pt(bzq)(CN)(CNtBu)] (bzq = benzo[h]quinolinate), were stacked into separate layers on glass (Fig. 2b and Fig. 2c) and pumped by a UV LED in a remote-phosphor configuration (Fig. 2a).

White light with photometric and chromatic parameters suitable for lighting applications was generated by these devices (Fig. 2d. Sicilia, V *et al. Applied Materials & Surfaces* 2016, 8, 16160-16169).

3) Chemosensors for the real-time detection of Hg2+ in water: The half-lantern dinuclear compounds $[\{Pt(bzq)(\mu\text{-}C_7H_4NSY\text{-}kN,S)\}_2]$ (Y = S (A), O (B)) [$C_7H_4NS_2$ = 2-mercaptobenzothiazolate, C_7H_4NOS

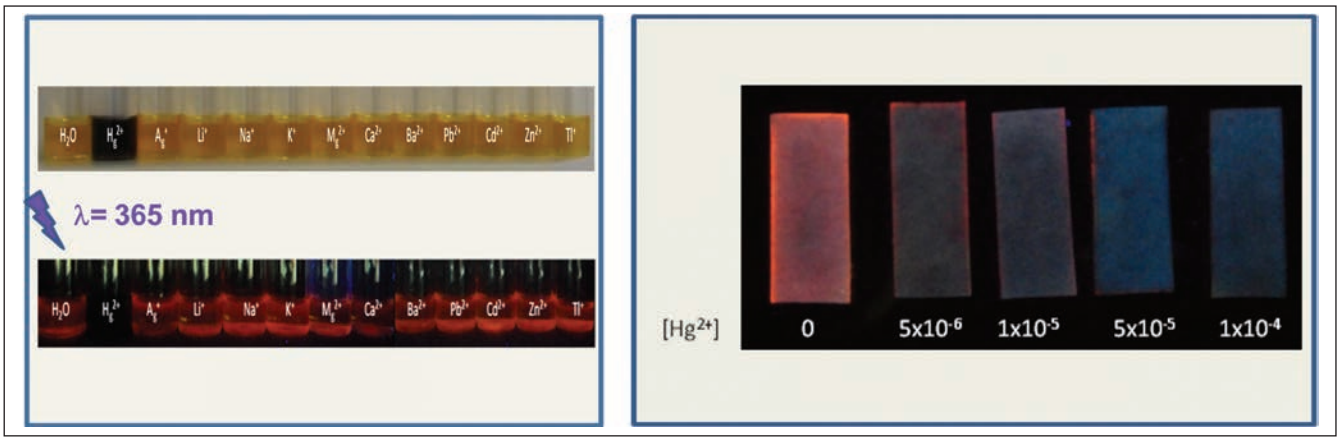

Fig. 3a (left) and 3b (right)

= 2-mercaptobenzoxazolate] show a yellowish-orange colour in a solution of DMSO/H_2O (5ml/0.5mL, 2x10^{-4} M, DMSO = dimethylsulfoxide) and intense red phosphorescence upon excitation with UV light (λ= 365nm, Fig. 3a).

The addition of 0.5mL of a diluted aqueous solution (0.01 M) of Hg^{2+} to them produces a striking colour change from yellowish-orange to purple, and the loss of their luminescence, while big amounts (up to 50:1) of environmentally relevant alkali and alkali-earth metal cations and other poisoning heavy-metal ones produce no change in their colour, their luminescence, nor interfere in the detection of Hg^{2+}. Therefore, these solutions could be used for the selective, naked eye detection of Hg^{2+} in water at concentrations as low as 2x10^{-6} M (See Fig. 3a).

Furthermore, test strips prepared by dipping filter paper in a solution of A/B in DMSO (2x10-4 M) and drying them in an oven suffer the loss of their luminescence when they are immersed in an aqueous solution containing Hg^{2+} in a concentration as low as 1x10^{-5} M, making complexes A and B good candidates for use as real-time Hg^{2+} sensors (See Fig. 3b).

The above-described colour and luminescence changes are also observable by UV-vis and emission spectroscopy with detection limits in the order of the micro-Molar (Sicilia, V *et al. Dalton Transactions* 2015, 44, 6936-6943).

4) An electronic nose: We are able to prepare new and different vapochromic compounds to be used as an electronic nose for VOCs (volatile organic compounds) and H_2O(v) detection. Thus,

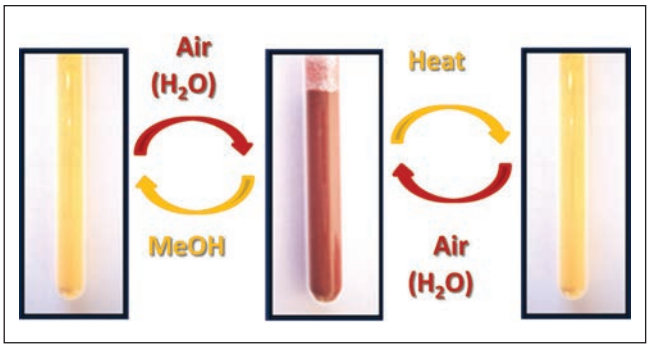

Fig. 4

compounds [K(H_2O)][Pt(C^N)($CN)_2$] (C^N = cyclometallated imines) were obtained as red or purple solids in the air. By heating them in the oven at 110°C, or gently heated under vacuum, the water molecules can be eliminated to give the anhydrous yellowish solids (see Fig. 4).

If the anhydrous forms are exposed to air, they pick up water molecules within seconds, becoming the hydrated forms. Moreover, yellowish samples of [K($S)_n$][Pt(bzq)($CN)_2$] can also be obtained by passing vapours of VOCs (S) such as methanol through thin-films of the red solid [K(H_2O)][Pt(bzq)($CN)_2$]. If these vapour-exposed samples are left in the air they restore their original colour (red) within seconds, showing a fully reversible vapochromic response.

Since the reversible transformation between the red and yellow forms is easily perceptible by the naked eye, these vapochromic compounds could be used as sensors to detect the presence of water and methanol vapours in the environment (Sicilia, V *et al. Inorg.Chem.* 2008, 47, 7166-7176).

My team collaborates with the Institute for Energy Research of Catalonia (IREC) and is open to collaborate with other public and/or private companies to execute scientific research and assistance in synthesis, characterisation and photophysical properties measurement, particularly of photoluminescent compounds, and create new ways of optimising molecular materials for new applications in the medium to long term.

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