



UNIVERSITA' DI MESSINA  
FACOLTA' DI SCIENZE

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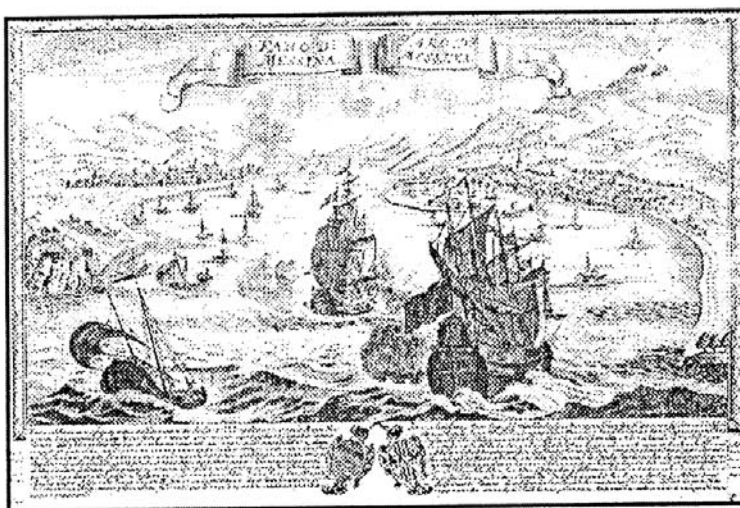
Società Chimica Italiana  
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Classe I di Scienze Fisiche  
Matematiche e Naturali

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



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## **LUMINESCENCE PROPERTIES OF PLATINUM(II) COMPLEXES**

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Excited state properties of transition metal complexes, in particular luminescence, are extensively studied because of both fundamental and applicative reasons. Solar energy conversion and information storage and treatment are research fields which are profoundly based on photoinduced energy and electron transfer processes involving metal complexes. While many efforts in transition metal photochemistry and photophysics have been devoted to  $d^6$  metals such as  $Ru(II)$  and  $Os(II)$ , the excited state properties of  $Pt(II)$  complexes have been investigated only at a minor extent.

Here the requirements for designing luminescent  $Pt(II)$  complexes are briefly discussed, along with some representative examples of known luminescent  $Pt(II)$  complexes. The compounds are adducts of  $[Pt(bpy)(NH_3)_2]^{2+}$  with crown ethers,  $Pt$ -cyclometallated species, and  $[Pt(LL)(X)_2]$  systems ( $bpy = 2, 2'$ -bipyridine;  $LL$ =chelating polypyridine species;  $X$ = halides,  $CN$ ).

Investigations on two new classes of luminescent  $Pt(II)$  complexes recently synthesized in our department are also

reported. The first class of compounds includes tight contact ion pairs of general formula  $\{Pt(R_2 - DTO)_2^{2+}, (X^-)_2\}$  ( $DTO$ =protonated dithioamide;  $R$ =benzyl,  $n$ -butyl, methyl, cyclohexyl;  $X = Cl, Br, I$ ). These species exhibit room temperature luminescence with lifetimes in the nanosecond time scale, originating from  $\sigma$ -bond  $Pt(d\pi)/S(p)$ -to- $\pi^*$  (dithioamide) charge transfer ( $SBLCT$ ) excited state ( $s$ ). The second class of complexes includes  $[Pt(R - terpy)X]^+$  and  $[Pt(R-terpy)Cl]^+$  complexes ( $R = H, Ph$ ;  $X = CH_3, Ph$ ). They exhibit 77 K long-lived (microsecond time scale) luminescence from ligand-centered ( $LC$ ),  $Pt(d\pi)$ -to- $terpy(\pi^*)$  charge transfer ( $MLCT$ ) and/or  $Pt - Pt(d\sigma^*)$ -to- $terpy(\pi^*)$  charge transfer ( $Pt_2$ -to- $terpy$ ) levels.  $Pt - Pt(d\sigma^*)$  orbitals are formed from the antibonding interaction between  $dz^2$  orbitals of two  $Pt(II)$  metal ions. Coupling origins from intermolecular interactions of head-to-tail stacked molecules. ( $Pt_2$ -to- $terpy$ ) luminescence can here be regarded as a probe of the stacking interaction.

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