Bis(2,9-diphenyl-1,10-phenanthroline)copper(I): a Copper Complex with a Long-lived Charge-transfer Excited State

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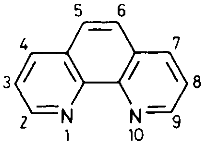
The title compound, $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline), exhibits long-lived emission at room temperature in solution, and, in contrast with copper(I) complexes of less bulky ligands, the emission persists in polar media; a water soluble derivative of $[Cu(dpp)_2]^+$ is luminescent at room temperature in aqueous solution and undergoes efficient redox photochemistry in the presence of electron acceptors.

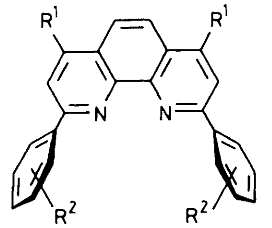
An important goal in inorganic photochemistry is to find ways to maximize excited state lifetimes. An interesting observation is that ring substituents have a pronounced effect on the excited state lifetimes of 1,10-phenanthroline (phen) (**1**) complexes. Thus derivatives of $[Cr(phen)_3]^{3+}$ bearing methyl or phenyl groups at the 4 and 7 positions exhibit ^2E states whose lifetimes are about twice that of the parent complex.[1] In the case of the analogous Ru^{II} system introducing methyl substituents in the 4 and 7 positions also doubles the lifetime of the lowest-lying charge-transfer excited state in solution, while phenyl substituents increase the lifetime by a factor of *ca.* 5.[2] The positional dependence of the substituent effect is marked. Typically, smaller lifetime enhancement attends substitution at the 5 and 6 positions.[1,2] Introducing methyl groups at the 2 and 9 positions sharply *decreases* the lifetime of $[Ru(phen)_3]^{2+}$.[3] Hitherto, the physical basis of these substituent effects has not been well understood. Here we report a striking substituent effect in a Cu^I system which can be explained mainly by steric considerations.

The finding that rhodium and iridium complexes of 2,9-dimethylphenanthroline (dmp) act as efficient catalysts for the water gas shift reaction[4] has initiated the search for synthetic routes to other 2,9-disubstituted phenanthrolines; although 2,9-diphenylphenanthroline (dpp) (2) has been mentioned in the literature,[5] it was only recently that its synthesis on a preparative scale has been reported.[6] The salts $[Cu(dpp)_2]BF_4$, $[Cu(tpp)_2]BF_4$, $[Cu(bcp)_2]BF_4$, and $[Cu(dmp)_2]BF_4$ were prepared by literature methods[7,8] [tpp = 2,4,7,9-tetraphenylphenanthroline (3), bcp = 2,9-dimethyl-4,7-diphenylphenanthroline]. Relevant photophysical data are reported in Table 1; absorption and emission spectra for the dpp and dmp complexes are presented in Figure 1. As has been discussed in detail for $[Cu(dmp)_2]^+$ the visible absorption and emission spectra can be assigned to metal-to-ligand charge-transfer excited states in all cases.[7,9] It should be noted that the absorption of the dpp complex extends well into the red, and that several distinct transitions occur; this property has been applied in the development of a photoelectrochemical cell displaying a very large spectral response.[10]

The results reported in Table 1 differ from those described above for the Ru^{II} and Cr^{III} complexes in several important respects. The decrease in the lifetime of $[Ru(phen)_3]^{2+}$ which occurs on introducing methyl groups at the 2 and 9 positions is believed to result from inter-ligand steric repulsions which decrease the effective ligand field strength, facilitating relaxation *via* higher-lying metal centred excited states.[3] With one fewer ligand involved, these repulsions do not occur in the Cu^I system, and the lifetime and the emission quantum yield are actually enhanced by replacing methyl groups with phenyl groups. Another contrast is that introducing phenyl groups at the 4 and 7 positions does not significantly change the lifetime for the Cu^I systems. The reasons for these differences are not obvious except that in view of the discussion below, substituents in the 2 and 9 positions are likely to increase greatly the overall rigidity of the molecule and to protect the metal centre from the solution environment.



(1); phen



(2) R^1 = H, R^2 = H; dpp
(3) R^1 = Ph, R^2 = H; tpp
(4) R^1 = H, R^2 = SO_3Na; dpp-S

Table 1. Photophysical data for $[Cu(NN)_2]^+$ systems in CH_2Cl_2 at 25 °C.

$[Cu(NN)_2]^+$	$\lambda_{abs.}$/nm (ϵ/dm^3 mol^{-1} cm^{-1})	$\lambda_{em.}$/nm[a]	τ/ns	$\phi \times 10^4$
$[Cu(dmp)_2]^{+b}$	454 (7950)	670	90	1.5
$[Cu(bcp)_2]^{+b}$	478 (13200	685	80	1.4
$[Cu(dpp)_2]^+$	439 (3200)	675	310	4.2
$[Cu(tpp)_2]^+$	450 (6400)	695	230	4.0

[a] Uncorrected emission maxima. [b] J. R. Kirchhoff, R. E. Gamache, Jr., M. W. Baskie, A. A. Del Paggio, R. K. Lengel, and D. R. McMillin, *Inorg. Chem.*, accepted for publication.

More important than the lifetime enhancement in CH_2Cl_2, the phenyl substituents render the excited state less susceptible to quenching by Lewis bases (Table 2). Whereas the addition of a few percent of MeOH almost completely quenches emission from $[Cu(dmp)_2]^+$ in CH_2Cl_2, $[Cu(dpp)_2]^+$ is emissive in pure MeOH. This unusual quenching may be a consequence of an associative reaction between a Lewis Base and the 'copper(II)' centre of the photoexcited complex, as previously suggested.[9,11] Consistent with this hypothesis, a space-filling model of $[Cu(dpp)_2]^+$ suggests that the central metal is well shielded by the phenyl substituents and that these groups would inhibit the approach of another ligand. The fact that 2,6-dimethylpyridine is a poorer quencher for $[Cu(dmp)_2]^+$ than pyridine lends additional support to the model.

The introduction of phenyl groups at the 2 and 9 positions also has a considerable effect on the solution photochemistry. For example, the yield for the photoinduced reduction of $[Co(NH_3)_6]^{3+}$ in a mixed water–tetrahydrofuran solvent at pH *ca.* 5 is enhanced about 500 times if a sulphonated derivative of $[Cu(dpp)_2]^+$ is used in place of the analogous derivative of $[Cu(bcp)_2]^+$. This water soluble derivative $[Cu(dpp\text{-}S)_2]^+$ [dpp-S = (4)] is luminescent at room temperature in aqueous solution (λ_{em} 680 nm), the excited state lifetime being τ *ca.* 70 ns. To our knowledge, $[Cu(dpp\text{-}S)_2{}^+]$ represents the first

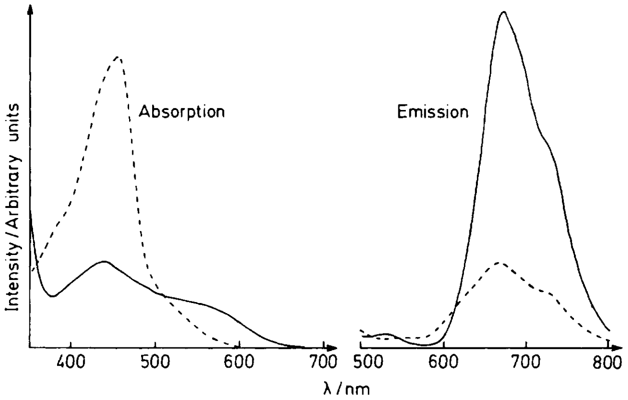


Figure 1. The absorption and emission spectra of $[Cu(dmp)_2]^+$ (- - - - -) and $[Cu(dpp)_2]^+$ (———) in CH_2Cl_2 at 25 °C.

Table 2. Stern–Volmer quenching constants determined at 25 °C.[a,b]

$[Cu(NN)_2]^+$	Quencher	K_{SV}/dm^3 mol^{-1}
$[Cu(dmp)_2]^+$	MeOH	2
$[Cu(dpp)_2]^+$	MeOH	c
$[Cu(dpp)_2]^+$	Pyridine	c
$[Cu(dmp)_2]^+$	Pyridine	80
$[Cu(dmp)_2]^+$	2,6-Dimethylpyridine	c

[a] The Stern–Volmer plots reveal a slight upward curvature, but this complication does not affect our basic conclusions. [b] The MeOH studies were carried out in CH_2Cl_2; the pyridine studies in 1,2-dichloroethane. [c] Too small to measure for quencher concentrations below 5% by volume; the upper limit for K_{SV} can be estimated to *ca.* 10^{-2} dm^3 mol^{-1}.

example of a copper(I) complex emitting in water at room temperature from a metal-to-ligand charge-transfer excited state.

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