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Luminescence Properties of Organometallic/Coordination Oligomers and Polymers Containing Diphosphine and Diisocyanide Assembling Ligands: Comparison between Mononuclear Model Complexes and Polymers

Pierre D. Harvey

Département de chimie, Université de Sherbrooke, Sherbrooke, PQ, Canada, J1K 2R1
E-mail: pierre.harvey@usherbrooke.ca

Summary: This paper describes the luminescence properties of selected examples of homo- and mixed-bridging ligand-containing organometallic/coordination oligomers and polymers of copper(I), silver(I), palladium(I) and –(0.5), and platinum(0.5). The bridging ligands are the 1,8-diisocyano-p-menthane (dmb) and bis(diphenylphosphino)methane (dppm), -ethane (dppe), -propane (dppp), -butane (dppb), -pentane (dpppen), and –hexane (dpph), as well as bis(diphenylphosphino)acetylene (dpa) and bis(dimethylphosphino)methane (dmpm). The comparison between the mononuclear model complexes and the polymers of the emission maxima (λ_{max}) and emission lifetimes (τ_e) will be made, and interpreted by the presence of intrachain interactions and exciton phenomena.

Keywords: copper; diisocyanides; diphosphines; emission lifetimes; exciton; luminescence; palladium; platinum; photophysics; silver

Introduction

The areas of organometallic/coordination polymers as well as crystal engineering and supramolecular assemblies have become extremely active in the past decade. Applications in the fields of supported catalysis, non-linear optics (NLO), light emitting diodes (LED), conducting and photoconducting materials are among the few examples of motivation for these researches. The luminescence properties are important for

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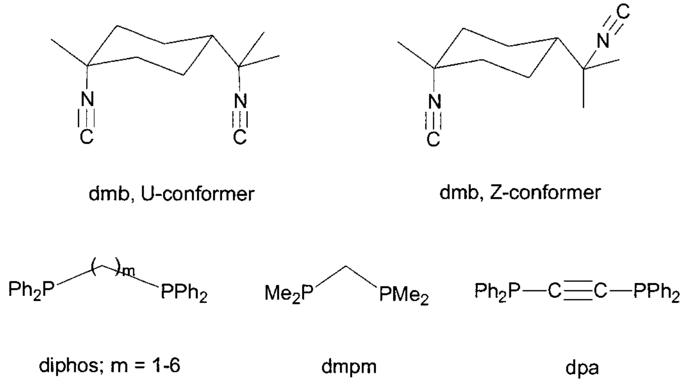
sensorizations and display devices, as well as LED applications, and their report in the literature are frequent (see recent examples on copper (I), silver (I), and platinum(0) see ref.[1-17]). However, their reports focus primarily on the luminescence spectroscopic and photophysical characterizations of the materials. In depth investigations on what effect their luminescence properties have, and on the excited state relaxation mechanism, are rather scarce.

We now wish to report a series of results that address the difference between the photophysical properties of the mononuclear complexes used as models for a single unit of a polymer, versus the corresponding polymers or oligomers. The list of bridging ligands is shown in Scheme 1.

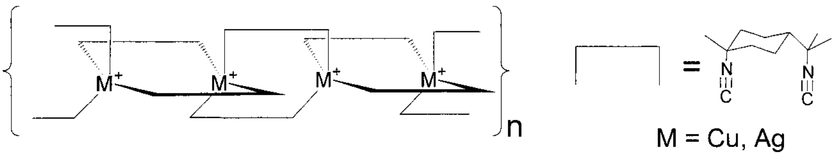


Scheme 1

Background

In 1992, this group reported a new type of coordination/organometallic polymer based on silver(I) and bridging ligand dmb.[18] The cationic polymers exhibit a 1-D structure and is of the type $\{Ag(dmb)_2]Y\}_n$ ($Y^- = BF_4^-$, PF_6^-, NO_3^-) where the dmb ligand adopts the U-conformer. The result was unprecedented because there was, no precedent for the preparation of polymers using this ligand, as recently reviewed.[19] Polymers of the type $\{Ag(Z\text{-}dmb)_2]Y\}_n$ and $\{Ag(U\text{-}dmb)(Z\text{-}dmb)]Y\}_n$ where $Y^- = TCNQ^-$ (teracyano-quinodimethane anion) have also been reported.[20] The silver atoms in $\{Ag(U\text{-}dmb)_2]Y\}_n$

(Y^- = BF_4^-, PF_6^-, NO_3^-) are tetracoordinated by four isocyanide groups forming a distorted geometry where the CAgC angles deviate strongly from the ideal tetrahedral angle of 109.45° according to X-ray for the PF_6^- salt, presumably due to intraligand steric hindrance.[19] The Ag···Ag distance is about 5 Å, and the Ag_3 angle is 140°. Subsequently, the Cu analogues were prepared and fully characterized, and the photophysical properties were also reported in detail as well.[21] Both types of polymers, Cu- and Ag-, are strongly luminescent in the solid states and in solution at 77 K in ethanol for example (λ_{max}(Cu) = 548 nm; λ_{max}(Ag) = 502 nm). The key feature is that the emission bands are very broad (FWHM = 150 nm) and the plots of ln of the luminescene intensity after an excitation pulse as a function of delay time (i.e. emission decay curves) are not linear, which are normally typical for unimolecular processes. The fact that the decay curves superimposed very well for solid state and solution data indicated that this unusual property was due to an intrachain phenomena. This behavior was identified as an exciton property,[22] and triggered an exhaustive investigation of the photophysical properties of organometallic /coordination polymers of copper(I), silver(I), palladium(I) and –(0.5), and platinum(0.5) (Scheme 2).



$\{M(dmb)_2^+\}_n$

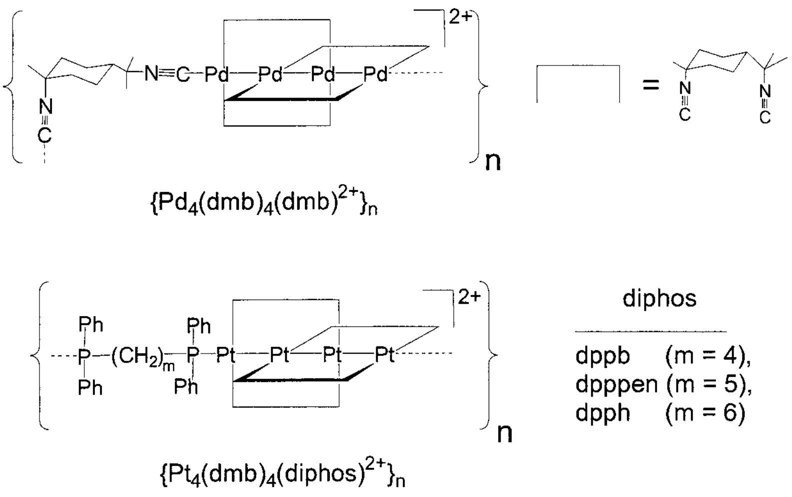
Scheme 2

Emission Data Analysis

The emission lifetimes can be analyzed in two ways. The first way was the common deconvolution method allowing for analysis of the raw data using models from 1 to 4 exponential decays. For unimolecular processes, the plots are linear and the slopes are related to the lifetimes (slope = $-1/\tau_e$). For multi-processes (bi-, tri- and tetraexponentials), the results provide both the lifetimes and the relative weight for each component. The second way is the ESM (Exponential Series Method),[23, 24] and consists of calculating a decay curve that may be composed of many components (up to 200 instead of only 4) with a window of calculated lifetimes well exceeding the time window of the data, insuring that any short or long components can be detected. Again the results are presented as lifetimes and relative weights, and the plots of lifetime versus weight represent the lifetime distribution. A single lifetime event gives a very narrow distribution. The quality of the fit between the experimental and calculated curves are also addressed using parameter χ (goodness-of-fit), and from the residual analysis. A good fit is accompanied with a residual where the "noise" above and under the baseline is evenly distributed.

The Polymers of Bi- and Tetranuclear Clusters

In 1997, Zhang et al reported the syntheses and characterization of new tetranuclear clusters of palladium and platinum formulated as $M_4(dmb)_4(PPh_3)_2^{2+}$ (M = Pd, Pt).[25, 26] Both types were unique because for palladium it was the first time that a 58-valence electron palladium cluster was reported. In addition, this M_4-cluster was linear, and a catenate sub-structure involving two interlocking "$Pd_2(dmb)_2$" rings using three Pd-Pd bonds (1 inner, and 2 outer), occurred (Scheme 3). Similarly for platinum, the same unprecedented features were noted, except that some other rare example of 58-electron species were already known. The X-ray structures for both species were reported, and the M-M bonds are as follows: for $Pd_4(dmb)_4(PPh_3)_2^{2+}$, d(Pd-Pd) = 2.534(13) inner, and 2.524(10) Å outer; for $Pt_4(dmb)_4(PPh_3)_2^{2+}$, d(Pt-Pt) = 2.641(2) inner, and 2.654(2) and 2.666(2) Å outer. For both cases, polymers of clusters have been prepared and fully characterized using crystallographic (for the red zig-zag shape $\{Pd_4(dmb)_4(Z\text{-}dmb)^{2+}\}_n$) and spectroscopic methods, and using molecular weight measurements (intrinsic viscosity for the amorphous orange $\{Pt_4(dmb)_4(diphos)^{2+}\}_n$; diphos = dppb, MW_n = 203 000; dpppen, MW_n = 307 000; dpph, MW_n = 84 000).



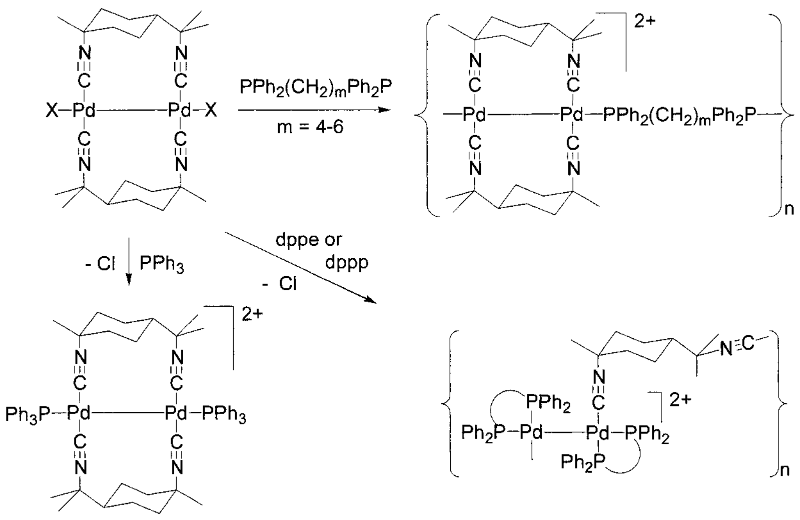
Scheme 3

Both series of polymers exhibit a lowest energy excited state of the type dσ→dσ* and are luminescent at 77K (Table1). Numerous comparisons can be made. First, the λ_{max} appears to be dependent upon whether it is a polymer versus the Pd_4-cluster species. The Pd_4-polymer structureless emission band is slightly more red-shifted by about 15 nm than the Pd_4-cluster. This result may reflect the difference in electron donating ability of the isocyanide versus phosphine, where the alkyl isocyanide is a stronger electron donor that PPh_3. On the other hand, such a comparison is not possible in the Pt_4-containing series. Variations are observed, but the phosphines are relatively similar. However, a red-shift of the emission band is observed going from dppb to dpppen to dpph. This trend may reflect that the CH_2-containing groups, more electron donating the phosphine, is. Some solvent effect is noted, where the use of PrCN leads to a red-shift of the emission maximum, as well as a decrease in lifetimes. Perhaps the most interesting feature is the change in emission lifetimes going from the cluster to its corresponding polymers; an approximate 2-fold increase is noted for both series. This increase is unexpected when considering the well-known “loose bolt” effect, where an increase in excited state deactivation is anticipated due to an increase in internal conversion associated with molecular vibration.[22] This result is better explained by the restriction in molecular motion of the chromophore. When the cluster is free to move, then excited state deactivation is enhanced. On the other hand, when the cluster is attached at both ends, the free rotation and torsion are much more restricted, leading to a lesser extent to excited deactivation.

Table 1. Photophysical data for the $M_4(dmb)_4^{2+}$-containing species.

Materials[a]	λ_{max} nm	τ_e ns	Conditions
$[Pd_4(dmb)_4(PPh_3)_2]^{2+}$	684	0.67 ± 2	77K/EtOH
$[Pd_4(dmb)_4(PPh_3)_2]^{2+}$	685	0.56 ± 1	77K/PrCN
$\{[Pd_4(dmb)_4(Z\text{-}dmb)]^{2+}\}_n$	698	1.14 ± 5	77K/EtOH
$\{[Pd_4(dmb)_4(Z\text{-}dmb)]^{2+}\}_n$	703	1.00 ± 2	77K/PrCN
$[Pt_4(dmb)_4(PPh_3)_2]^{2+}$	750	2.71 ± 5	77K/EtOH
$\{Pt_4(dmb)_4(dppb)\}_n$	736	4.78 ± 5	77K/EtOH
$\{Pt_4(dmb)_4(dpppen)\}_n$	750	5.15 ± 5	77K/EtOH
$\{Pt_4(dmb)_4(dpph)\}_n$	755	5.17 ± 5	77K/EtOH

Recently, a second and original series of new polymers of polynuclear palladium series has been reported.[27-29] This series is divided into two series: 1) $\{Pd_2(dmb)_2(diphos)^{2+}\}_n$ (diphos = dppb, dpppen, dpph, and dpa), which are red,[27, 28] and 2) $\{Pd_2(diphos`)_2(dmb)^{2+}\}_n$ (diphos` = dppe, dppp), which are yellow. Both series are prepared from the d^9-d^9 binuclear complex $Pd_2(dmb)_2Cl_2$ (Scheme 4).[28, 29] The materials in the solid state are amorphous based upon XRD measurements, and no X-ray crystallographic data could be obtained, despite numerous attempts. Based upon the intrinsic viscosity measurements, the *MW*n for $\{Pd_2(dmb)_2(diphos)^{2+}\}_n$ are 17 800 (dppb, ~14 units), 18 400 (dpppen, ~14 units), 16 100 (dpph; ~12 units), and 19 500 (dpa, ~ 12 units), and for $\{Pd_2(diphos`)_2(dmb)^{2+}\}_n$ the *MW*n are 11800 (dppe, ~8 units) and 12 100 (dppp, ~8 units).



Scheme 4

The complex $Pd_2(dmb)_2(PPh_3)_2^{2+}$ can be used as a comparison molecule. The lowest energy excited state is also of the type dσ→dσ*. This complex and the oligomers are not luminescent in solution nor in the solid state at room temperature, and may be associated with an energy wasting photo-induced hemolytic Pd_2-bond scission or ligand dissociation in the excited state. However, the compounds become luminescent at 77 K (in PrCN). The $Pd_2(dmb)_2(PPh_3)_2^{2+}$ complex and the $\{Pd_2(dmb)_2(diphos)^{2+}\}_n$ oligomers (diphos = dppb, dpppent, dpph, dpa) exhibit emission maxima (λ_{max}) between 627 and 638 nm (Table 2). The excitation spectra superpose the absorptions relatively well, indicating that the absorbing and emitting species are the same. The emission λ_{max} data are more red-shifted in comparison with those observed for the $\{Pd_2(diphos')_2(dmb)^{2+}\}_n$ oligomers ($500 < \lambda_{max} < 509$ nm), which is consistent with the more blue-shifted dσ→dσ* absorptions of the latters (diphos'= dppe (414), dppp (400)). The Stokes shifts (difference between the absorption and emission maxima; Δ) are in the order of 4 500 to 5 600 cm^{-1}, suggesting that the luminescence is phosphorescence. However, the ns timescale is strikingly short, but not unprecedented. For example, the luminescence of the related

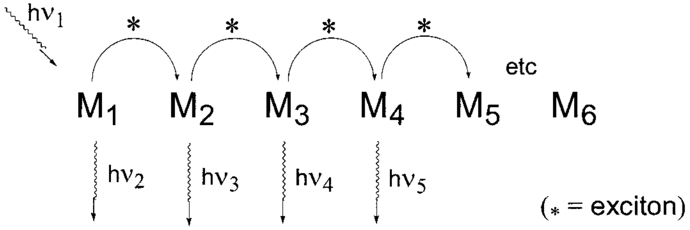
$Pd_2(dmb)_2Cl_2$ dimer exhibits a τ_e of 71 ± 6 ns at 77 K.[30] On the other hand, the ns timescale is also too long to be assigned to a fluorescence (the fluoresecence lifetime for 4d- and 5d-containing chromophore is generally in the ps time scale). The former assignment is preferred. The emission quantum yields appear constant for most species ($0.12 < \Phi < 0.17$), which is consistent with the similarity in τ_e data, but three of them listed in Table 2 (diphos = dppb, dpppen, dpph) exhibit 2 to 8 fold decreases. This difference is unexplained at the moment.

Table 2. Spectroscopic and photophysical data for the oligomers in PrCN at 77K.

Compounds	λ_{max}	Δ	τ_e	Φ
	nm	±100 cm^{-1a}	± 0.08 ns	± 10%
$[Pd_2(dmb)_2(PPh_3)_2](ClO_4)_2$	627	4 900	2.75	0.14
$\{[Pd_2(dmb)_2(dppb)](ClO_4)_2\}_n$	632	5 100	1.87	0.026
$\{[Pd_2(dmb)_2(dppen)](ClO_4)_2\}_n$	634	5 200	2.70	0.071
$\{[Pd_2(dmb)_2(dpph)](ClO_4)_2\}_n$	636	4 900	2.24	0.046
$\{[Pd_2(dmb)_2(dpa)](ClO_4)_2\}_n$	638	4 800	2.30	0.15
$\{[Pd_2(dppet)_2(dmb)](ClO_4)_2\}_n$	509	4 500	1.94	0.13
$\{[Pd_2(dpppro)_2(dmb)](ClO_4)_2\}_n$	508	5 300	1.50	0.12

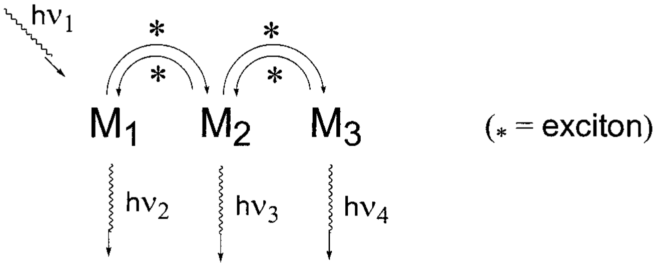
The 1-D dmb-Polymers of Copper(I) and Silver(I)[21]

A brief introduction on the $\{M(dmb)_2^{2+}\}_n$ polymers (M = Cu; Ag) is presented above,[18-21] and further relevant information on their properties can be found in the following ref.[31-34] The emission spectra are broad (~150 nm) and centered around 550 and 500 nm for M = Cu and Ag, respectively. The graphs of the ln of luminescence intensity as a function of delay time after the light pulse (decay curve) is not mono-exponential. It is, in fact, non-exponential. An examination of the emission spectra as a function of delay time (time-resolved emission spectroscopy) indicates the presence of an "infinite" number of discrete emission bands contributing to the overall spectral envelope. By comparing the slopes in the decay curves and the λ_{max} of emission in the time-resolved spectra at the early event after the pulse with those obtained for the mononuclear complexes $M(CN\text{-}t\text{-}Bu)_4^+$ (M = Cu, Ag) as model compounds for a single chromophore unit, one readily depicts the close resemblance. This important information indicates that at the early event after the light pulse, the chromophore $M(CN\text{-}t\text{-}Bu)_4^+$ absorbs the light and luminesces as a "non-interacting species". As time evolves, other and slower photophysical events occur with red-shifted emissions. Because of the fact that the decay traces are almost identical for the polymers in the solid state and in solution, one come to the conclusion that this photophysical process occurs within the chain. Because of this multiple emission behavior, it is not surprising that the emission light is found depolarized. This process is known as an exciton phenomenon (Scheme 5).



Scheme 5

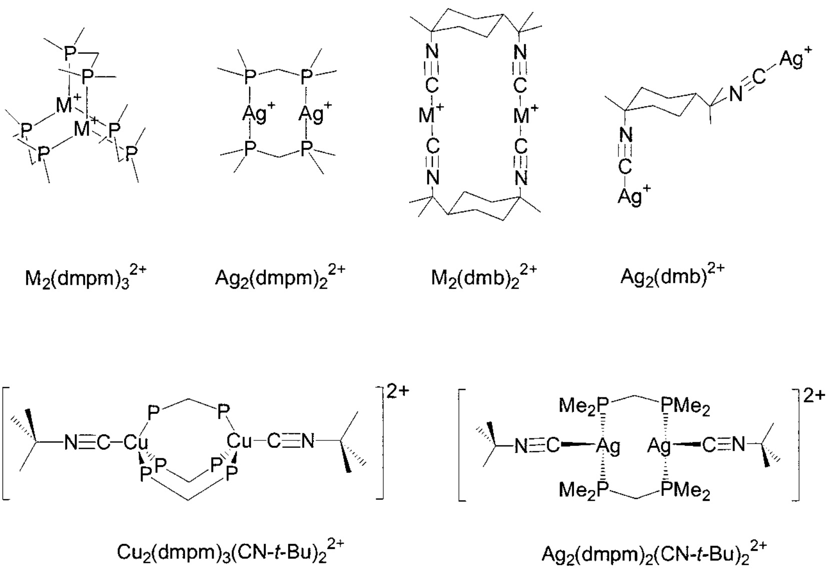
Based on DFT calculations, the lowest energy excited state of the $M(CN\text{-}t\text{-}Bu)_4^+$ chromophore is a metal-to-ligand-charge-transfer (MLCT). Based on the X-ray data of the $\{Ag(dmb)_2^{2+}\}_n$ polymers, the N···N distance is in the range of 4.3 Å,[33] a distance that is close to the sum of the van der Waals radii (3.4-3.6 Å), and sufficiently short for weak interactions and energy transfer to occur. Normally, exciton phenomena are important in the singlet state for organics because of the selection rule, but in the triplet state, this property should not be important. In fact, for metal-containing species, spin-orbit coupling renders the selection rule less rigorous, and such a process becomes possible. One of the key features is the knowledge of the molecular dimension of the $\{M(dmb)_2^{2+}\}_n$ polymers in solution (M = Cu, number of units = 300;[21] M= Ag, number of units = 8).[34] The fact that the X-ray structure for $\{Ag(dmb)_2^{2+}\}_n$ demonstrates the presence of a polymer, not an oligomer of 8 units, is also striking because the photophysical data are almost identical, as stated above. This observation indicates that energy transfer is reversible (Scheme 6), which is consistent with the fact that the chromophores are identical (no donor and acceptor). The questions are now to what extent this energy delocalisation takes places, and how can they be fine-tuned.



Scheme 6

The Small dmb-Oligomers of Copper(I) and Silver(I)

In an attempt to control the molecular dimension of the interacting Cu- and Ag-containing chromophores, small oligomers have been synthesized.[35] Indeed, the luminescent binuclear complexes $M_2(dmpm)_3^{2+}$ (M = Cu, Ag), $Ag_2(dmpm)_2^{2+}$ and $Cu_2(dmpm)_3(CN\text{-}t\text{-}Bu)_2^{2+}$ (as BF_4^- salts), as well as the oligomers described as $\{Cu_2(dmpm)_3(dmb)_{1.33}{}^{2+}\}_3$ and $\{Ag_2(dmpm)_2(dmb)_{1.33}{}^{2+}\}_3$, have been prepared and fully characterized in the solid state. These binuclear compounds and small oligomers bear the chromophore units $M_2(dmpm)_3^{2+}$, $Ag_2(dmpm)_2^{2+}$, $M_2(dmb)_2^{2+}$ (M = Cu, Ag) and $Ag_2(dmb)^{2+}$ (Scheme 7), and exhibit emission maxima ranging from 445 to 485 nm with emission lifetimes found in the μs regime.



Scheme 7

The time-resolved emission spectra for the oligomers and the known polymers $\{M(dmb)_2{}^{+}\}_n$ (M = Cu, Ag) also exhibit blue-shifted emission bands at the early stage of the photophysical event after the light pulse, which also red-shift with longer delay times (Figure 1).

The decay traces are more or less exponential as well exemplified shown in Figure 2. In this graph, $[Cu_2(dmpm)_3(CN\text{-}t\text{-}Bu)_2](BF_4)_2$ exhibits a relatively linear decay, indicating the poor extent of exciton delocalisation. On the other hand, the decay trace for the $\{Cu(dmb)_2{}^{2+}\}_n$ polymer (here 45 units), exhibits a non-exponential behavior.

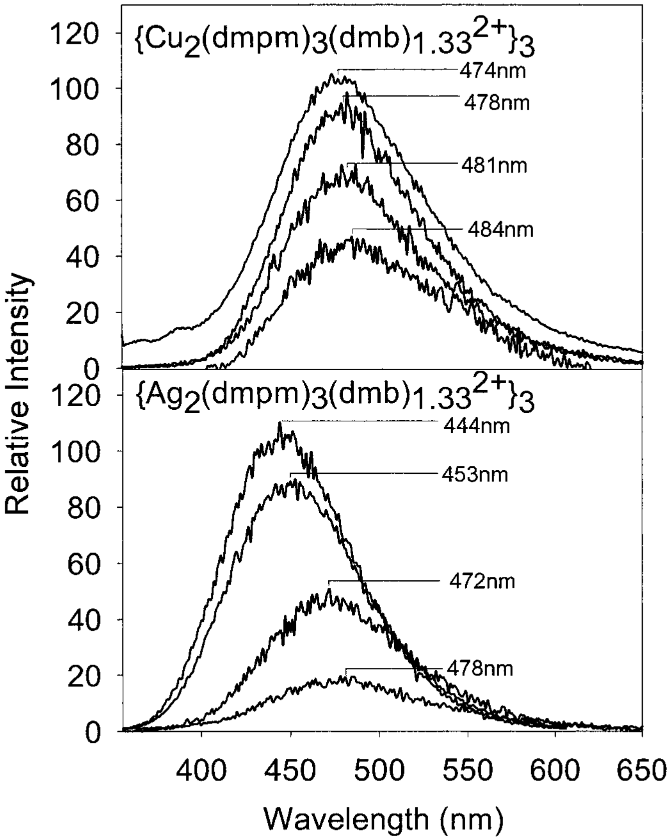


Figure 1. Time-resolved emission spectra for solid $\{Cu_2(dmpm)_3(dmb)_{1.33}{}^{2+}\}_3$ (above) and $\{Ag_2(dmpm)_2(dmb)_{1.33}{}^{2+}\}_3$ (below) at room temperature. The measurements have been made in the following time frames: for above: 474 nm, 20-70; 478, 500-600; 481, 1 000-1 300; 484; 2 000-2 500μs; for below: 444 nm, 20-70; 453, 300-400; 472, 500-600; 478, 1 000-1 300 μs.

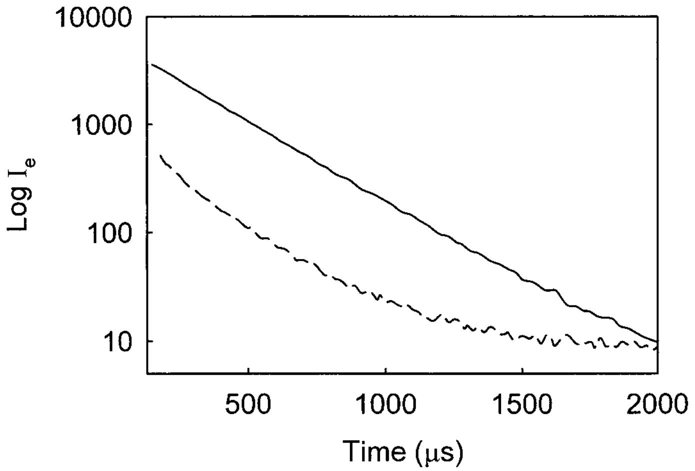


Figure 2. Solid state decay traces for the emission of $[Cu_2(dmpm)_3(CN\text{-}t\text{-}Bu)_2](BF_4)_2$ (—) versus $\{Cu(dmb)_2{}^+\}_n$ (----) at 298K.

These non-exponential decay traces were analyzed by ESM and exhibit a distribution of lifetimes that can be fairly broad as exemplified in Figure 3. It is interesting to note that the width of the distribution is a function of the number of units in the chain. The comparison is crude because the nature of the emissive excited state is not the same for all three examples. For $Ag_2(dmpm)_2{}^{2+}$, the lowest excited state is dσ*-pσ,[36-42] not MLCT. So the electronic transition is confined within the M_2P_6 or M_2P_4 unit, which are of a smaller dimension in comparison with "$M(CN)_x$" chromophores. Hence, the shortest interchromophore distance may not be the same from one system to another. The extent of red-shift of the emission band with delay time and the fwhm (full-width-at-half-maximum) of the distribution of lifetimes also appears to increase as the number of M_2-units increases in the oligomers. This behavior is also consistent with an exciton process, as described above.

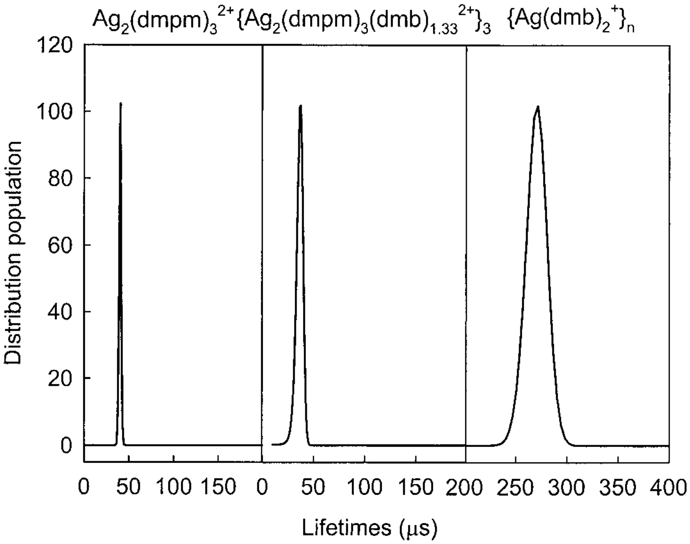


Figure 3. Comparison of the distribution of lifetimes fitting emission decay traces for solid $Ag_2(dmpm)_2^{2+}$, $\{Ag_2(dmpm)_2(dmb)_{1.33}^{2+}\}_3$ and $\{Ag(dmb)_2^+\}_n$ (n = 8) at 298K.

Conclusion

This paper focused on demonstrating that there is a clear difference between the properties of discrete complexes and organometallic/coordination polymeric materials. Evidence for inter-unit interactions, steric or excitonic, is present, and these properties clearly modulate the overall optical properties of the bulk. Knowing this, fine tuning of the photophysical properties for NLO, LED and digital display applications appears possible in this way.

Acknowledgments

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