For $BaPd(CN)_4$, in contrast to the Pt salt, the emission lifetimes should be more characteristic of a $^1A_{2u} \rightarrow {}^1A_{1g}$ electric-dipole spin-allowed transition and a $^3A_{2u} \rightarrow {}^1A_{1g}$ spin-forbidden transition because of a smaller spin–orbit constant. Thus, the spin-allowed lifetime should be shorter than with Pt and the spin-forbidden lifetime for Pd longer than for Pt; again, this is in agreement with experimental data.

Acknowledgment. This work has been supported by the National Science Foundation, Material Science Division (Grant DMR77-07140). Also, the authors wish to acknowledge Mr. Brad Cort for growing the crystals used in this study.

Registry No. $BaPd(CN)_4$, 14038-83-6.

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Luminescence Spectra of Some Substituted Group 6B Metal Carbonyls in Methane and Argon Matrices at 12 K

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Received March 26, 1980

The importance of the matrix-isolation technique for the measurement of emission and excitation spectra of $M(CO)_5L$ complexes (M = Mo and W; L = pyridine, 3-bromopyridine, pyridazine, piperidine, NH_3, PMe_3, and PCl_3) has been demonstrated. For the first time both fluorescence and phosphorescence emission have been detected. Only phosphorescence was found for $Mo(CO)_5py$, and for the Cr complexes no luminescence was obtained. The fluorescence band shifted to higher energy upon going from N-donor to P-donor complexes corresponding to the shift of the lowest-lying d–d transition in the UV–visible absorption spectrum. $W(CO)_5pyr$, which has a low-lying MLCT transition, showed no detectable luminescence in contrast to emission studies in glasses at 77 K.

Introduction

Photochemistry of substituted group 6B metal carbonyls both in solutions[1-10] and in matrices at 12 K has been the subject of several papers.[11-19] For these complexes two photochemical pathways are found (eq I and II). The

$$M(CO)_5L \xrightarrow{\lambda,\, L'} M(CO)_5L' + L \tag{I}$$

$$M(CO)_5L \xrightarrow{\lambda',\, L'} M(CO)_4LL' + CO \tag{II}$$

pathways are dependent on the wavelength of irradiation, the metal, and the ligand L. A higher quantum yield of CO ejection was found after short wavelength irradiation and/or in going from M = W to Mo and Cr.[7] A drastic reduction of quantum efficiency is found when a MLCT transition is lowest in energy for ligands having low-lying π^* orbitals.[4] For the photochemical processes I and II the total reaction quantum yield was less than unity, showing that radiative and nonradiative deactivation processes must be involved. Information about such deactivation processes is sparse, and only for a few substituted metal carbonyl complexes, e.g., $XRe(CO)_3L$ (X = Cl, Br, I; L = 9,10-phenanthroline and related ligands),[20-22] $W(CO)_4$(substituted pyridine)$_2$,[23,24] $M(CO)_4$bpy (M = Cr, Mo, W),[25] and $W(CO)_5L$ (L = donor ligands (amines, ethers, ketones, and phosphines))[1,3-5,8-10] has luminescence been reported, mostly in glasses at 77 K. Matrix isolation has been very successful in characterising the intermediates and elucidating the photochemical pathways. However, in going from solutions at room temperature to matrices at 12 K, the photochemical behavior changes.[19] For a more detailed understanding of the photochemistry of substituted metal carbonyls it is therefore necessary to investigate deactivation processes.

In this paper we describe the results of luminescence measurements of a series of $M(CO)_5L$ complexes (M = Mo and W; L = pyridine, 3-bromopyridine, pyridazine, piperidine, PMe_3, and PCl_3) in Ar and CH_4 matrices at 12 K; some preliminary results have been reported earlier.[26]

Results

A. UV–Visible Spectra. The UV–visible absorption spectra of the $W(CO)_5L$ complexes (L = amine, imine) show one

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Table I. Emission Maxima (nm) for $M(CO)_5L$ Complexes in Gas Matrices and Glasses with Intensities in Parentheses[a]

	Ar (12 K)		CH_4 (12 K)		glass (77 K)	
complex	$^1E_a \rightarrow {}^1A_1$	$^3E_a \rightarrow {}^1A_1$	$^1E_a \rightarrow {}^1A_1$	$^3E_a \rightarrow {}^1A_1$	$^1E_a \rightarrow {}^1A_1$	$^3E_a \rightarrow {}^1A_1$
$Mo(CO)_5py$		517 (m)		522 (w)	*c*	*c*
$W(CO)_5py$	424 (w)	523 (s)	420 (w)	525 (s)		510, 523[c]
$W(CO)_5(3\text{-Br-py})$	424 (w)	531 (m)	422 (w)	534 (m)		529[c]
$W(CO)_5py$						581[d]
$W(CO)_5pip$	424 (w)	524 (m)	426 (w)	525 (m)		533[c]
$W(CO)_5PMe_3$	369 (w)		371 (w)		*b*	*b*
$W(CO)_5PCl_3$	367 (w)		367 (w)			≈530[e]

[a] Relative emission intensities (vw = very weak, mw = medium weak, w = weak, m = medium, s = strong) were obtained of samples with comparable absorbances (0.2–1.0 od units). These intensity data must be interpreted with care, because of differences in volatility and extinction coefficients. [b] Data not available. [c] Data from ref 4, in methylcyclohexane and EPA glasses. [d] Data from ref 8, in a 2,3-dimethylbutane/*n*-pentane glass. [e] Data from ref 5, no details of the glass available.

Table II. Absorption and Excitation Maxima (nm) of $M(CO)_5L$ Complexes in Matrices at 12 K

	absorption				
complex (matrix)	CT	d-d	MLCT	intraligand	excitation
$Mo(CO)_5py(Ar)$	227	281 (sh), 284, 305, 368	322		374, 396
$Mo(CO)_5py(CH_4)$	227	282, 284 (sh), 307, 370	325		378, 396
$W(CO)_5py(Ar)$	235	284, 375, 438	346		372, 394, 437
$W(CO)_5py(CH_4)$	235	284, 375, 438	346		376, 400, 448
$W(CO)_5(3\text{-Br-py})(Ar)$	238	284, 386	348		325 (sh), 400, 450 (sh)
$W(CO)_5(3\text{-Br-py})(CH_4)$	238	285, 386	348		396
$W(CO)_5pyr(Ar)$	238	284, 330, 360 (sh), 393	427		*a*
$W(CO)_5pyr(CH_4)$	*b*	*b*	*b*		*b*
$W(CO)_5pip(Ar)$	242	274, 294, 330, 372, 393, 400, 442			377, 388, 408
$W(CO)_5pip(CH_4)$	*b*	282, 330, 374, 395, 401, 402			371, 388, 405
$W(CO)_5PMe_3(Ar)$	244	330		219	335
$W(CO)_5PMe_3(CH_4)$	245	330		220	*a*
$W(CO)_5PCl_3(Ar)$	220	285,[c] 320 (sh), 340, 375 (sh)	238		325
$W(CO)_5PCl_3(CH_4)$	220	285,[c] 320 (sh), 340, 375 (sh)	238		330

[a] No excitation data could be obtained. [b] Data not available. [c] The absorption of about 280 nm is assigned to a d-d transition for the $M(CO)_5L$ complexes with the exception of $W(CO)_5PCl_3$. The 285-nm band of $W(CO)_5PCl_3$ is due to a M → T*(CO) transition. Weak bands of $M(CO)_6$ in the UV absorption spectrum could not be avoided for some $M(CO)_5L$ complexes, due to a small amount of decomposition.

intense M → π*(CO) charge-transfer band at about 240 nm. Several d → d transitions are detected in the region 260–400 nm. The most intense of these transitions has been assigned (C_{4v} symmetry) to the $^1E_a(b_2^2e^3a_1^1) \leftarrow {}^1A_1(b_2^2e^4)$ transition.[27] The weak band which is only observed for the W complexes at about 440 nm is assigned to $^3E_a \leftarrow {}^1A_1$. For the complexes with L = pyridine, 3-bromopyridine, and pyridazine the MLCT transitions overlap with a d → d transition. In going from N-donor ligands to P-donor ligands the d → d and the M ← π*(CO) CT bands are shifted to higher energies due to the π-back-bonding property of the P-donor ligands.

B. Luminescence Spectra. All $W(CO)_5L$ complexes (L = N donor) showed two emission bands with maxima at about 420 and 520 nm in CH_4 and Ar matrices. The latter band has been detected in low-temperature glasses and attributed to spin-forbidden phosphorescence, $^3E_a \rightarrow {}^1A_1$, supported by lifetime measurements.[1,3,4,8,9] A phosphorescence lifetime of 3.4 ± 0.2 μs has been measured for $W(CO)_5py$ in argon, in good agreement to that obtained previously at 77 K in a hydrocarbon glass (methylcyclohexane; 2.5 μs)[28] and in EPA (5:5:2 by volume of diethyl ether:isopentane:ethanol; 0.86 μs).[4] The 420-nm emission band, which was not observed in low-temperature glasses, was found for all N-donor W complexes. From the position of the 420-nm emission band relative to the $^1E_a \leftarrow {}^1A_1$ d → d transition in the absorption spectrum, we assign this band to fluorescence ($^1E_a \rightarrow {}^1A_1$). Figure 1 shows the absorption and luminescence spectra of $W(CO)_5pip$ in methane and argon matrices. No detectable emission was found for $W(CO)_5pyr$, $Mo(CO)_5pip$, and a series of $Cr(CO)_5L$

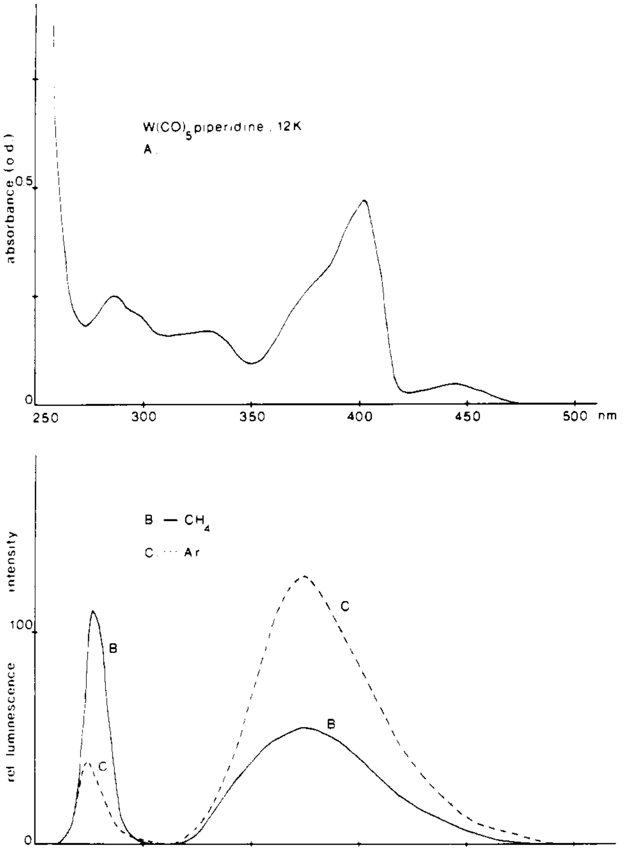

Figure 1. Absorption (A) and emission spectra of $W(CO)_5pip$ isolated at 12 K in (B) methane and (C) argon matrices.

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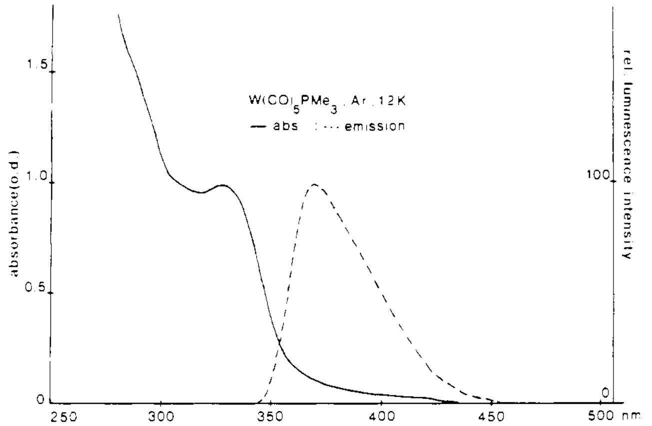
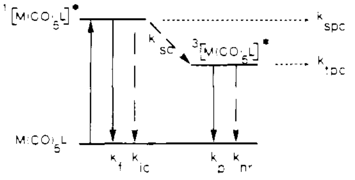


Figure 2. Absorption (—) and emission (---) spectra of $W(CO)_5PMe_3$ isolated in an argon matrix at 12 K.

Scheme I. Singlet and Triplet Energy Levels with Associated Rate Constants[a]



[a] k_f and k_p are respectively the rate constants for fluorescence and phosphorescence; k_{spc} and k_{tpc} are respectively the rate constants for photochemistry from excited singlet and triplet levels; k_{ic}, k_{isc}, and k_{nr} are respectively the rate constants for internal conversion, intersystem crossing, and nonradiative decay from the triplet.

complexes (L = N donor, P donor) in argon and methane matrices. Only one weak luminiscence band at about 370 nm was observed for $W(CO)_5PMe_3$ (Figure 2) and $W(CO)_5PCl_3$, which we assign to $^1E_a \rightarrow {}^1A_1$ fluorescence in agreement with the observed fluorescence of $W(CO)_6$.[26] Excitation spectra ($\lambda_{em} \approx 520$ nm) were measured for complexes with a high emission intensity. The excitation maxima obtained are in good agreement with the d → d absorption maxima, showing that the radiative processes are due to the $M(CO)_5L$ complexes and not to impurities. The luminescence data are presented in Table I and the absorption and excitation data in Table II.

Discussion

In going from solutions at room temperature to hydrocarbon glasses at 77 K and to matrices at 12 K differences are found for the photochemical and photophysical processes of the $M(CO)_5L$ complexes. For discussion of these differences Scheme I[29] will be used. The emission lifetimes (τ) and quantum yields (ϕ) can be expressed by eq 1–4. It has been

$$\tau_f = (k_f + k_{ic} + k_{isc} + k_{spc})^{-1} \quad (1)$$

$$\tau_p = (k_p + k_{nr} + k_{tpc})^{-1} \quad (2)$$

$$\phi_f = k_f\tau_f \quad (3)$$

$$\phi_p = k_{isc}\tau_f k_p \tau_p \quad (4)$$

established that k_{ic} and k_{nr} are temperature dependent, whereas k_f and k_p are not.[30] Thus upon going to lower temperatures the emission processes become competitive with the nonradiative decay processes, and emission is observed. Similarly the emission lifetimes should increase upon going to lower temperatures. The fluorescence lifetime may be estimated from eq 5.[31] By substitution of ϕ_f of the order of 10^{-2} at 12

$$\tau_f = \phi_f\tau_{rad} = \phi_f(10^{-4}\epsilon_{max}^{-1}) \quad (5)$$

K and ϵ_{max} of the order of 5000, we obtain $\tau_f \simeq 200$ ps. At higher temperatures, ϕ_f will decrease, causing a comparable decrease in τ_f. At room temperature fluorescence has not been observed, indicating a quantum yield $<10^{-4}$ and a lifetime of the order of 2 ps. The small Stokes shift of ca. 1300 cm^{-1} observed in this study is consistent with fluorescence from a Franck–Condon state.[32]

Upon going from a CH_4 matrix to an Ar matrix the fluorescence emission intensity from $W(CO)_5pip$ (Figure 2) decreases, and the phosphorescence intensity increases. A similar effect has been observed for the fluorescence and phosphorescence emissions of C_6H_6 in CH_4 and Ar matrices at 12 K.[33] In C_6H_6 this has been shown to be the result of enhanced intersystem crossing due to the external heavy-atom effect. We propose that the fluorescence quenching of $W(CO)_5pip$ upon going from CH_4 to Ar matrices is due to the same effect. In Kr matrices the fluorescence of $W(CO)_5pip$ is completely quenched, and the phosphorescence is further enhanced compared to Ar matrices; an identical effect has been found for C_6H_6 in Kr.[33]

In previous studies in hydrocarbon glasses at 77 K no emission was detectable from $M(CO)_5L$ (M = Mo, Cr; L = N donor) complexes.[3] In CH_4 and Ar matrices at 12 K emission was not observed from $Cr(CO)_5L$ (L = pyridine, piperidine) nor $Mo(CO)_5pip$; however emission has been observed for the first time from $Mo(CO)_5py$. This emission is tentatively assigned to $^3E \rightarrow {}^1A_1$ phosphorescence, corresponding to the phosphorescence of $W(CO)_5py$.

In the case of $W(CO)_5pyr$ in Ar and CH_4 matrices no emission was detectable. In contrast to the other amines and imine complexes the longest wavelength transition for this complex is of MLCT character in nonpolar solvents. In EPA at 77 K emission has been observed from $W(CO)_5L$ complexes (L = 4-benzoylpyridine, 4-acetylpyridine, 4-cyanopyridine, and 4-formylpyridine), which similarly all have a MLCT transition lowest in energy in nonpolar solvents.[4] In view of the well-characterized shift of the MLCT transition to higher energy in polar solvents,[4] we consider it likely that the emission observed in EPA at 77 K is not from the MLCT state but is $^3E \rightarrow {}^1A_1$ phosphorescence as in the case of $W(CO)_5py$. The failure to detect emission from $W(CO)_5pyr$ in CH_4 and Ar matrices at 12 K can be attributed to the very rapid nonradiative internal conversion process $^1MLCT \rightarrow {}^1A_1$.[34]

In accordance with the increase of π-back-bonding character of P-donor ligands compared to N-donor ligands a blue shift of 4000–5000 cm^{-1} was found in the absorption spectra for the d → d transitions in $W(CO)_5$(P-donor) complexes relative to $W(CO)_5$(N-donor) complexes. Corresponding to this shift the fluorescence maximum shows a shift to higher energy of similar magnitude. No phosphorescence was detectable in CH_4 and Ar matrices at 12 K for $W(CO)_5$(P-donor) complexes. However in glasses at 77 K only phosphorescence has been previously observed at the same wavelength as from N-donor ligands.[5] Unfortunately no details of the glasses used were given, but a phosphorimeter was used to measure the emission

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(29) The nature of the excited state, MLCT or d–d, does not affect the general validity of this scheme.

(30) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, London, 1970.

(31) C. A. Parker, "Photoluminescence of Solutions", Elsevier, Amsterdam, 1968, p 22. It has been shown by Birks (ref 30, p 120) that in general the use of eq 5 to estimate excited-state lifetimes is valid to within 10%. It must be pointed out that eq 5 was derived for atomic and not polyatomic species.

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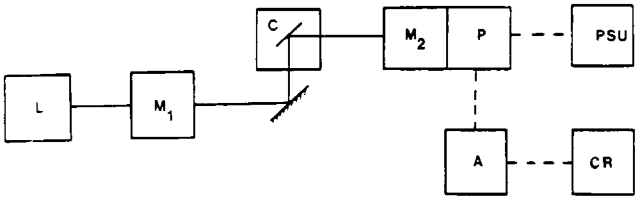

Figure 3. Block diagram of emission spectrometer used in this study. The light path is shown as a continuous line and the electrical connections as dotted lines. Details of the components are as follows: L = 450-W Xe arc lamp; M_1 = Bausch and Lomb high-intensity monochromator; C = cryostat head with cold LiF window; M_2 = Spex Minimate; P = RCA 1P28 photomultiplier tube; PSU = Brandenburg 476R regulated power supply unit; A = Keithley 414S picoammeter; CR = Tekman TE200 chart recorder.

spectra, and thus fluorescence would not have been detected. The lack of detectable phosphorescence at 12 K leads us to suggest that the previously reported emission at about 530 nm is not due to the phosphorus donor complex but to possible photolysis or decomposition products.

The lack of detectable phosphorescence from W(CO)$_5$PMe$_3$ and W(CO)$_5$PCl$_3$ can be interpreted as showing that the lowest triplet state is not appreciably populated and therefore that the photochemistry of W(CO)$_5$L complexes proceeds primarily via the lowest singlet state. This indicates that internal heavy-atom induced spin–orbit coupling is not important in the case of tungsten P-donor complexes and that differences in photochemical yields for unique ligand ejection and CO exchange in M(CO)$_5$L complexes (M = Cr, Mo, W) are due to differences in the rates of internal conversion between the $d_{x^2-y^2}$ and d_{z^2} σ^* orbitals.[7] Further work is in progress to determine emission lifetimes and quantum yields in order to calculate photophysical and photochemical rate constants for such systems.

Experimental Section

All M(CO)$_5$L complexes were prepared with use of standard literature methods, with only slight modifications, as published earlier.[1-10,14-16] The purity of the complex was checked by infrared spectroscopy and by elemental analysis. The vacuum system and the equipment used to achieve cryogenic temperatures have been described extensively together with the gas deposition system.[15] Matrix gases with a purity of BOC grade X were used. Initial experiments were carried out, with use of infrared spectroscopy (Grubb-Parsons Spectromajor infrared spectrometer) in order to determine spray-on conditions to obtain well-isolated species. Typically, matrix to sample ratios of about 2000:1 were used. Deposition temperatures varied between −5 °C for W(CO)$_5$PMe$_3$ and 70 °C for W(CO)$_5$(3-Br-py) and spray-on times varied from 60 to 200 min, in order to obtain an absorbance of 0.2 to 1.0 for the lowest-lying d → d transition. UV-visible absorption spectra were recorded on a Pye Unicam SP 1800 spectrometer. Emission and excitation spectra were recorded on a homemade spectrometer, the details of which are given in Figure 3. The emission monochromator was regularly calibrated with use of a medium pressure mercury lamp. Reproducibility of the results was checked by measuring the spectra of each complex several times. The following precautions were taken to ensure that the detected luminescence came from the complex. (a) Photolysis of the sample by the excitation wavelength was reduced by blocking off the radiation between measurements with different exciting wavelength. The extent of any photolysis was monitored by running infrared spectra before and after the luminescence measurements. (b) Experiments with matrix gases alone or with possible photolysis products, e.g., M(CO)$_4$py, showed no detectable emission. (c) No emission was detectable upon exciting at wavelengths outside the observed absorption bands of the M(CO)$_5$L complexes. The phosphorescence lifetime of W(CO)$_5$py in an argon matrix at 12 K was measured with use of the time-correlated single-photon-counting technique.[35,36]

Acknowledgment. The authors wish to express their thanks to J. v.d. Helm and W. G. J. de Lange for preparing some of the metal complexes. The University of Southampton, the SRC, and the Royal Society are thanked for grants (to A.J.R.). We also thank the British Council for support under the Academic Links Scheme.

Registry No. Mo(CO)$_5$py, 14324-76-6; W(CO)$_5$py, 14586-49-3; W(CO)$_2$(3-Br-py), 17000-12-3; W(CO)$_5$pyr, 65761-20-8; W(CO)$_5$pip, 31082-68-5; W(CO)$_5$PMe$_3$, 26555-11-3; W(CO)$_5$PCl$_3$, 21223-85-8.

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New Luminescent Quantum Counter Systems Based on a Transition-Metal Complex

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Received April 18, 1980

New luminescent quantum counter systems based on tris(2,2′-bipyridine)ruthenium(II) chloride dispersed in either poly(vinyl alcohol) (PVA) or poly(vinylpyrrolidone) (PVP) solid films are described. While these new systems have a somewhat more limited wavelength range (≤540 nm) than the ever-popular Rhodamine B quantum counters (≤600 nm), their sensitivity is double that of the standard Rhodamine B counter and their response vs. wavelength can be flatter. The films have only been calibrated to 360 nm, but solution work indicates that they should be useful to ~280 nm. Further, the films are easier to handle than the dye solutions.

Introduction

The term "quantum counter" was originally used by Bowen in 1936[1] to describe an optically dense fluorescent screen placed before a detector. With selection of a luminescent material having an emission spectrum and photon yield which were independent of excitation wavelength, the response of the composite system was quantum flat (i.e., equal phototube current for the same flux in photons per second) within the absorbing range of the dye. Bowen originally found crystalline uranyl ammonium sulfate in paraffin (252–436 nm) and aqueous aesculin (252–367 nm) to be quantum flat within the accuracy of his measurements.

Luminescent quantum counters did not acquire popularity until after 1955 when Melhuish[2] introduced optically dense solutions of the dye Rhodamine B (RhB). This dye is now known to be nearly quantum flat in response for the range 250–600 nm.[3-5] Luminescent quantum counters are now

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