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Observations of intermolecular excimers in several π-conjugated polymers and exciplexes of these polymers with tris(*p*-tolyl)amine are reported. It is shown that the luminescence of conjugated polymer thin films originates from excimer emission and that the generally low quantum yield is due to self-quenching. Thus in sufficiently dilute solution, the "single-chain" emission has a quantum yield of unity. Exciplex luminescence and exciplex-mediated charge photogeneration have much higher quantum yields than the excimer-mediated photophysical processes. These results provide a new basis for understanding and controlling the photophysics of conjugated polymers in terms of supramolecular structure and morphology.

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by

Samson A. Jenekhe and John A. Osaheni

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EXCIMERS AND EXCIPLEXES OF CONJUGATED POLYMERS

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Observations of intermolecular excimers in several π-conjugated polymers and exciplexes of these polymers with tris(*p*-tolyl)amine are reported. It is shown that the luminescence of conjugated polymer thin films originates from excimer emission and that the generally low quantum yield is due to self-quenching. Thus in sufficiently dilute solution, the "single-chain" emission has a quantum yield of unity. Exciplex luminescence and exciplex-mediated charge photogeneration have much higher quantum yields than the excimer-mediated photophysical processes. These results provide a new basis for understanding and controlling the photophysics of conjugated polymers in terms of supramolecular structure and morphology.

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Conjugated polymers have attracted much research interest in science and technology in the past two decades (1-5). Conducting polymers (1-5), which are ground-state charge transfer complexes of conjugated polymers, are of wide interest as semiconductors and electroactive materials for diverse applications ranging from biosensors, batteries, and loudspeakers to molecular electronic devices (3-5). In their pristine form, π-conjugated polymers are of wide interest as third-order nonlinear optical materials for photonic switching devices (4,6,7) and as optoelectronic materials for light emitting diodes (8,9), solar cells (10), and xerographic photoreceptors (11). Exciplexes, which are charge transfer complexes that are stable only in the excited-state, represent important areas that are only recently being explored in conjugated polymers (12,13). Although there has been much theoretical and experimental work on the photophysics of conjugated polymers (14-18), including the nature of the excited states, origin of luminescence, and nature of charge photogeneration, the picture of these photophysical processes in conjugated polymers remains poorly understood and controversial (14-18).

One common way excimers (19-27) are formed is by interaction of an excited chromophore ${}^1A^*$ with an unexcited chromophore ${}^1A$: ${}^1A^* + {}^1A \rightleftharpoons {}^1(AA)^*$. Such an excited-state complex is stable due to resonance contributions from exciton and charge transfer configurations: ${}^1(A^*A) \leftrightarrow {}^1(AA^*) \leftrightarrow {}^1(A^-A^+) \leftrightarrow {}^1(A^+A^-)$. The corresponding excimer wave function is (21,23): $\Psi_{excimer} = c_1[\Psi(A^*A) + \Psi(AA^*)] + c_2[\Psi(A^-A^+) + \Psi(A^+A^-)]$. The ratio c_1/c_2 and hence the relative contributions from exciton and charge transfer may vary for different materials. Singlet exciplexes are formed similarly but from two distinct chromophores A (acceptor) and D (donor), either A or D is excited, i.e. ${}^1A^* + {}^1D$ or ${}^1A + {}^1D^* \rightarrow {}^1(A^-D^+)^*$, and similarly stabilized (21,24): ${}^1(A^*D) \leftrightarrow {}^1(AD^*) \leftrightarrow {}^1(A^-D^+)$. Studies (19-27) of excimers and exciplexes in small molecules have shown that their basic supramolecular structures are cofacial sandwich-type configurations with interplanar distances of 3-4 Å. Interestingly, π-conjugated polymers are generally stiff chain molecules with relatively planar geometries and very strong intermolecular interactions, leading to cofacial chain packing in the solid state (2,3,28,29). Intermolecular distances of 3.3-3.6 Å in sandwich-type cofacial packing have been determined by X-ray diffraction and by computational modeling of the supramolecular structure and morphology of many π-conjugated polymers (28,29). It is therefore reasonable to expect that excimers might efficiently form in excited π-conjugated polymers since the materials are already configured into potential excimer-forming sandwich-type supramolecular structures.

We report the formation of intermolecular excimers by a series of π-conjugated polybenzobisthiazoles (**1a** -**1g**), polybenzobisoxazole (**2a**), and poly(benzimidazobenzophenanthroline ladder) (**3**) shown in Figure 1. We also report the formation of intermolecular exciplexes between these polymers and tris(*p*-tolyl) amine (**4**). The formation and properties of excimers $^1(AA)^*$ and exciplexes $^1(A^-D^+)^*$, where A is a conjugated polymer chromophore and D is **4**, were investigated by steady-state and time-resolved fluorescence spectroscopy, picosecond transient absorption spectroscopy, and charge photogeneration in xerographic photoinduced discharge experiments. Dilute and concentrated fluid and solid solutions as well as thin films of these rigid chain polymers were investigated (30).

All photophysical measurements were done at room temperature. Optical absorption and excitation spectra of 10^{-7} to 10^{-3} M fluid solutions in methanesulfonic acid (MSA) and 10^{-3} to 12 M solid solutions in **5** were obtained (30). Steady state photoluminescence (PL) measurements were done on the same fluid and solid solutions as well as on thin films of the polymers. PL quantum yield Φ_f was measured by comparing the integration of the emission spectrum of a sample to a standard of known Φ_f under identical optical conditions (25,31,32). A 10^{-6} M quinine sulfate solution (0.1 N in H_2SO_4, $\Phi_f = 55\%$) (31) and a thin film of ~10^{-3} M 9,10-diphenylanthracene in poly(methyl methacrylate) ($\Phi_f = 83\%$) (32) were used as fluorophore standards for fluid solutions and thin films respectively. Picosecond time-resolved PL decay measurements were made by using the time-correlated single photon counting technique and laser system described elsewhere (12). The picosecond transient absorption spectroscopy is a typical pump and probe experiment described previously (33). Field-dependent quantum yield $\phi(E)$ for charge photogeneration was measured in the applied field range of 7 x 10^3 to 10^6 V/cm as described elsewhere (11).

The π-conjugated polymers in Figure 1 have very rigid chain structures (28-29) similar to highly fluorescent dye molecules (32). However, the measured fluorescence quantum yield Φ_f for thin films varied from 10^{-3}% for **3** to 10% for **2a**. These low values of quantum yield are very similar to those reported in other classes of conjugated polymers (3,8,9). To clarify the PL quenching in these polymers, the concentration dependence of Φ_f was measured for fluid and solid solutions. Figure 2 illustrates the typical results for fluid solutions of **1a** and **1d**, showing increase of PL quantum efficiency with decreasing concentration. The quantum yield in dilute solution ($\leq 10^{-6}$ M) is 100%, sharply decreasing to ~50% at 10^{-5} M, and to only 10-13% at 10^{-4} M. Approximately similar variation of quantum yield with concentration was observed in solid solutions of **1a** and **1d**. In thin films, the limiting Φ_f values of **1a** and **1d** were 6 and 5% respectively. These results suggest that the rather low PL quantum yield of thin films of these polymers is due to concentration or self-quenching. Furthermore, the observed high quantum yield in dilute solutions of all the polymers rule out intrachain interactions, torsional vibrations, defects along the chains, or impurities as important channels for nonradiative deactivation of the excited state. Therefore, we propose excimer formation as the intermolecular mechanism of concentration quenching and we use "excimer" here as the central concept even though the possibility that more than two chromophores are involved cannot be ruled out.

The ground-state absorption and excitation spectra of fluid and solid solutions of the polymers in a wide concentration range (10^{-7} to 10^{-3} M) were similar to the thin film spectra. The absorption spectra of **1a** at selected solution concentrations and in the solid state are shown in Figure 3A. In contrast to the absorption spectra which were similar at different concentrations, the emission spectra lineshape and peak changed dramatically with concentration. In dilute solution, the emission spectra showed well resolved vibronic structure (Figures 3B and 3C). The thin film emission spectra were generally broad, structureless, and red-shifted from the dilute solution spectra as exemplified for **1a** in Figures 3B and 3C. The progressive evolution of the broad and structureless emission of thin films from the highly structured emission spectra in dilute solutions was seen with increasing concentration in fluid or solid solutions. In dilute solid solution of **1a**, a mirror image relationship between the excitation and emission spectra is seen as often observed in small molecules (32). We interpret the dilute solution emission spectra of these polymers as those due to the singlet excited state of the "single chain" or "isolated chromophore" $^{1}A^{*}$. The emission from $^{1}A^{*}$ is not observed in the thin films; thus, we interpret the observed thin film emission of the conjugated polymers as originating from mainly singlet excimers, $^{1}(AA)^{*}$.

The time-resolved PL decay dynamics of dilute solutions of all the polymers exhibited a single exponential decay (Fig. 4A), indicating a single fluorescent species $^{1}A^{*}$. The measured lifetime of $^{1}A^{*}$ varied from 0.2 ns for **3** to 0.6 ns for **1a** and **1c**. The corresponding PL decay dynamics of thin films of the same polymers was found to be nonexponential (Fig. 4B), requiring two or three exponentials to fit the data. For example, the PL decay dynamics of **1a** thin film was best described by a biexponential with lifetimes of ~50 ps and ~500 ps. Multiexponential decay dynamics of thin films may be a result of complex kinetics that include distinct species of $^{1}(AA)^{*}$, $^{1}A^{*}$, and even different types of excimers and aggregated complexes.

The stabilization energy E_{λ} of the excimers in these polymers, which is the spectroscopic energy difference between the "single chain" $^{1}A^{*}$ (o-o line) and excimer $^{1}(AA)^{*}$ emission maxima (21,23), varied from 0.3 and 0.45 eV for **1b** and **1a**, respectively, to 0.5 eV for **3**. These E_{λ} values provide an explanation for the apparently large Stokes shift (~0.5 - 0.7 eV) of thin film emission spectra in that once E_{λ} is subtracted to account for excimer emission the true Stokes shift between the "single chain" emission (o-o line) and absorption becomes small (for example, 0.05 eV for **1a**) and comparable to values normally found in small molecules (25,32) (Figure 3C).

The triarylamine **4** (E_{D}^{ox} = 0.74 V versus saturated calomel electrode, SCE) which is known to form exciplexes with many conjugated aromatic molecules (34) was used as a probe donor molecule to investigate exciplex formation by the series of π-conjugated polymers. Donor (D)/acceptor (A) bilayer thin film assemblies were found to have absorption and excitation spectra that are composed of only the component spectra. The absence of the $4^{+\bullet}$ radical cation which absorbs strongly at ~680 nm proved the absence of ground-state interaction. Photoexcitation of the D/A bilayers thin films, at 355 nm, produced a strong transient absorption band at 680 nm due to $4^{+\bullet}$ in about 125 ps, suggesting the formation of excited-state charge transfer complexes. PL spectra of D/A bilayer thin films showed that they exhibited strong luminescence that was relatively broad and structureless (12), similar to the excimer emission of the pristine thin films. However, the emission from the D/A bilayers has two distinct features relative to the polymer thin film: (i) a blue shift; and (ii) a large enhancement of PL quantum yield by a factor of 3-4. In the case of **2a**, for example, this means that the PL quantum yield has been increased from 10% to 40% by excited-state charge transfer complex formation with 4.

The measured PL decay dynamics of the D/A bilayers was not monoexponential, similar to the observation on the pristine polymer thin films. However, the lifetimes of the D/A emitting states were significantly longer than those of the polymer thin films. This fact along with the steady state PL results suggested that the emitting state in these bilayers is the singlet exciplex $^1(A^-D^+)^*$. The blue shift (~0.16 - 0.28 eV) of the exciplex luminescence relative to the emission from the pristine polymer thin films is explained in terms of the smaller stabilization energy of an exciplex compared to an excimer. The $^1(A^-D^+)^*$ exciplex emission is still red-shifted from the "single chain" $^1A^*$ emission in accord with the well-known behavior of molecular exciplexes and what should be expected from energetic considerations (20-25). In the absence of knowledge that the emission of the conjugated polymer thin films originates from excimers, the blue shift of the exciplex emission would be difficult to explain with the current models of the photophysics of π-conjugated polymers (14-18). Our explanation of the enhanced PL quantum yield of exciplex luminescence is that the quantum yield of radiative decay of $^1(A^-D^+)^*$ is significantly larger than of $^1(AA)^*$ and that exciplex formation efficiently competes for ${}^1A^*$ with excimer formation and self-quenching.

In the exciplex emission process, ${}^1(A^-D^+)^* \rightarrow (AD) + h\nu$, it has been shown in molecular exciplexes that a linear relationship holds between the exciplex emission maximum $h\nu$ and the redox properties (E_D^{ox}, E_A^{red}) of the components (21-24). Figure 5A shows that such a linear relationship approximately holds in exciplexes of conjugated polymers. This approach to tuning emission color has been successfully applied to the problem of achieving efficient blue luminescence in conjugated polymers for light emitting diode applications (12). With regard to electroluminescence in π-conjugated polymers (8,9), we point out that excimers and exciplexes discussed here can also be electrically generated through recombination of injected positive and negative charges (21,23,34): ${}^2A^- + {}^2A^+ \rightarrow {}^{1,3}(AA)^*$ and ${}^2A^- + {}^2D^+ \rightarrow {}^1(A^-D^+)^*$.

Photocarrier generation in the conjugated polymers in the forms of thin films of the pristine materials and D/A bilayers was measured by the xerographic photodischarge technique (11). The field-dependent quantum efficiency $\phi(E)$ for photogeneration of charge carriers was too small to be measurable in thin films of the pristine materials but was readily measured and found to be large in D/A bilayers of the polymers. For example, $\phi(E)$ varied from ~0.15% at low fields ($<10^4$ V/cm) to ~14% at 7 x 10^5 V/cm for **4/1b** bilayers photoexcited at 430 nm (Figure 5B). This strong dependence of photogeneration efficiency on applied field, wherein $\phi(E)$ varied by 2-3 orders of magnitude between ~10^4 to 10^6 V/cm, was generally observed. The highest $\phi(E)$ values were on the order of 30-50% at 10^6 V/cm, for instance in **4/1a** bilayers (11). These results can be understood in terms of excimers and exciplexes as the key photogenerated species in the pristine materials and the D/A bilayers respectively. Field-assisted dissociation of the excimers, ${}^1(AA)^* \rightarrow A^- + A^+$, proves to be an inefficient process. In contrast, field-assisted dissociation of the exciplexes, ${}^1(A^-D^+)^* \rightarrow A^- + D^+$, is intrinsically more efficient owing to the greater charge transfer in exciplexes and their dipole moment.

The observation of excimers and exciplexes in π-conjugated polymers opens up new vistas for theoretical and experimental understanding of the materials and for developing them for applications.

The preliminary picture of the photophysics of conjugated polymers that is emerging from our observations is the following. Excitons are produced on photoexcitation but they rapidly form excimers . Poor quantum yields of luminescence and photocarrier generation are consequences of excimer formation. Exciplex formation enhances quantum yields of the photophysical processes. Our results also suggest that the fundamental approach to efficient photophysical processes in conjugated polymers is through control of the supramolecular structure and morphology of the materials. For example, copolymerization and side group substitutions are some of the synthetic strategies that can be used to control interchain packing distances and degree of intermolecular excimer formation (35).

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30. The synthesis and characterization of the molecular and supramolecular structures of the conjugated polymers have been reported (28,29). These polymers are soluble in methanesulfonic acid (MSA) and nitromethane/$AlCl_3$ in which they form liquid crystalline phases at high solution concentrations (> ~5 - 10 wt%) due to their rigid rodlike conformations (29). Polymer thin films were prepared by spin casting from ~0.5 - 1.0 wt% solutions in nitromethane/$AlCl_3$ as previously described (28). Thin films of solid solutions of a conjugated polymer in poly(benzobisthiazole decamethylene) (5) were similarly prepared through solutions in nitromethane/$AlCl_3$. D/A bilayer thin films were prepared by first spin casting the conjugated polymer layer (A, 15-40 nm thick) followed by the D layer as previously described (11).

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FIGURE CAPTIONS

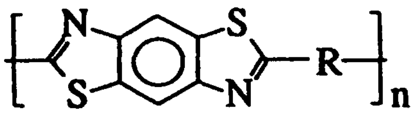
Figure 1. Structures of π-conjugated polymers (**1**, **2**, and **3**) and donor molecule **4** investigated.

Figure 2. Concentration dependence of photoluminescence quantum yield Φ_f of **1a** (dark circles) and **1d** (open squares) in fluid solution.

Figure 3. A - Optical absorption spectra of **1a** in fluid solution in MSA (1-3) and thin film (4): 1 = 1.5 x 10^{-6} M; 2 = 2.5 x 10^{-5} M; 3 = 1.0 x 10^{-4} M. B - Photoluminescence spectra of **1a** thin film (1) and in fluid solution in MSA: 2 = 5 x 10^{-3}; 3 = 1 x 10^{-4} M; 4 = 1.4 x 10^{-5} M; 5 = 3.6 x 10^{-6} M. All solution PL spectra correspond to excitation at 420 nm and the thin film spectrum is for 438 nm excitation. C - Excitation (1) and photoluminescence (2) spectra of 2 x 10^{-3} M **1a** in solid solution in **5** compared to emission of **1a** thin films (3). The excitation wavelengths for the PL spectra are 430 nm (2) and 438 nm (3).

Figure 4. A - Time-resolved PL decay dynamics of 10^{-6} M solution of **1a** in MSA, indicating a single exponential which was fitted with a lifetime of 0.6 ns. B - Time-resolved PL decay dynamics of **1a** thin film, indicating a biexponential data which was fitted with lifetimes of 50 ps and 500 ps.

Figure 5. A - Exciplex luminescence peak as a function of the difference between donor (**4**) oxidation potential and acceptor (π-conjugated polymer) reduction potential. The line is a least square fit to the data. B - Field-dependent quantum efficiency ϕ(E) for charge photogeneration in a **4**/**1b** bilayer photoexcited at the absorption band of **1b** (430 nm).



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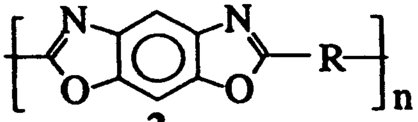

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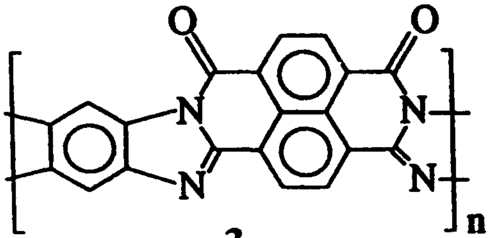

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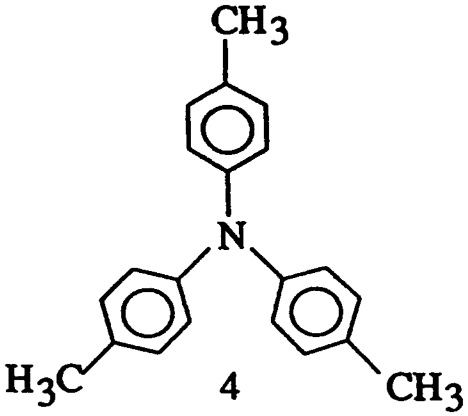

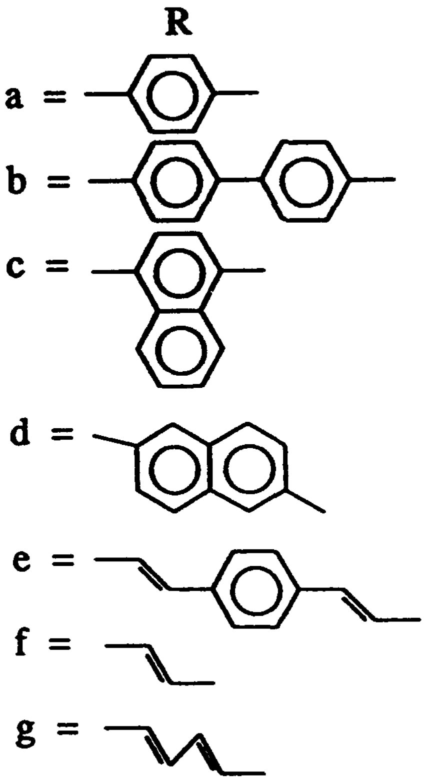

Figure 1

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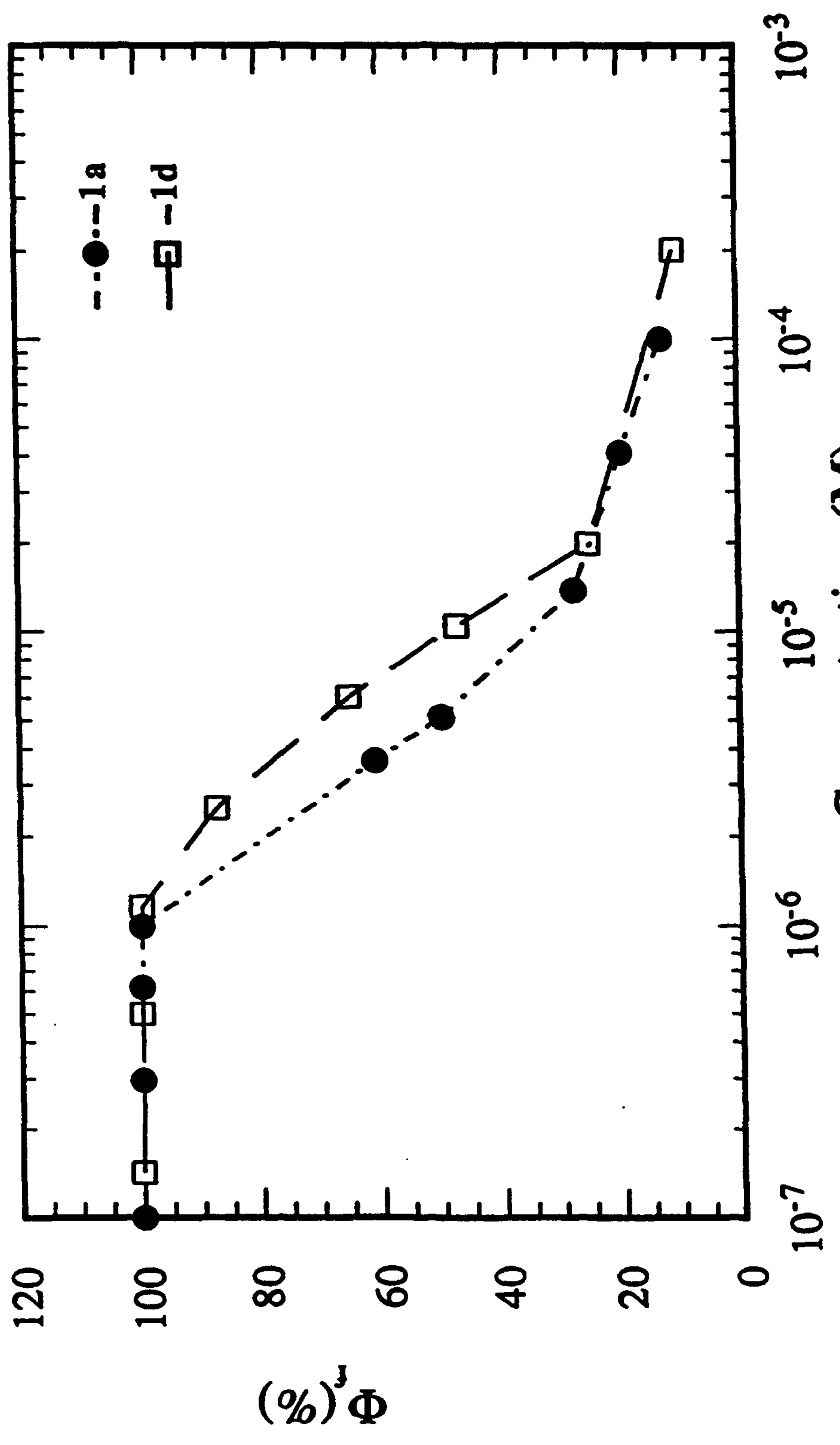
Fig. 2



Φ_f (%)
0
20
40
60
80
100
120
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
Concentration (M)
1a
1d

Fig. 3A

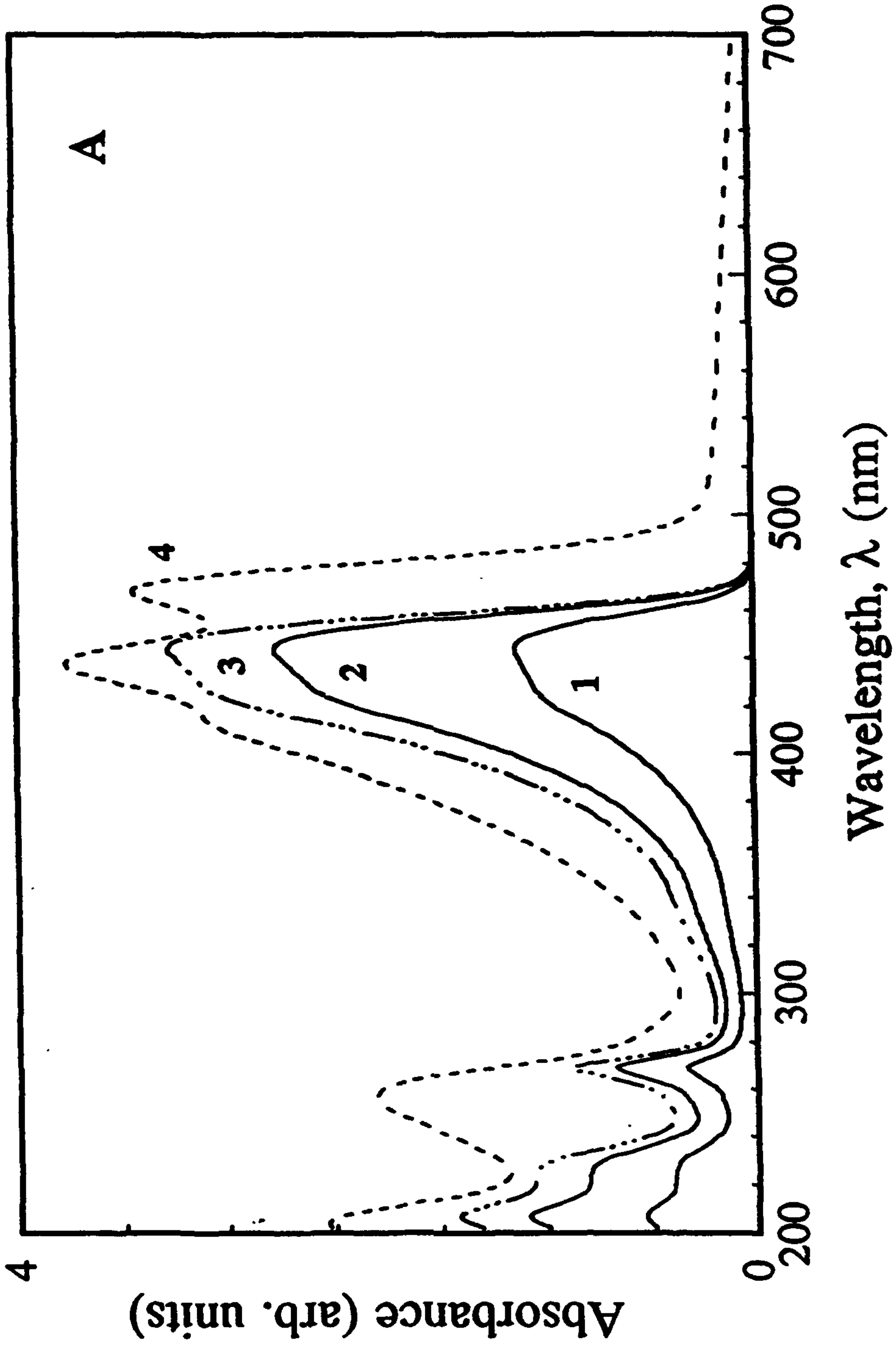

A
4
3
2
1
Absorbance (arb. units)
4
0
200
300
400
500
600
700
Wavelength, λ (nm)

Fig. 3B

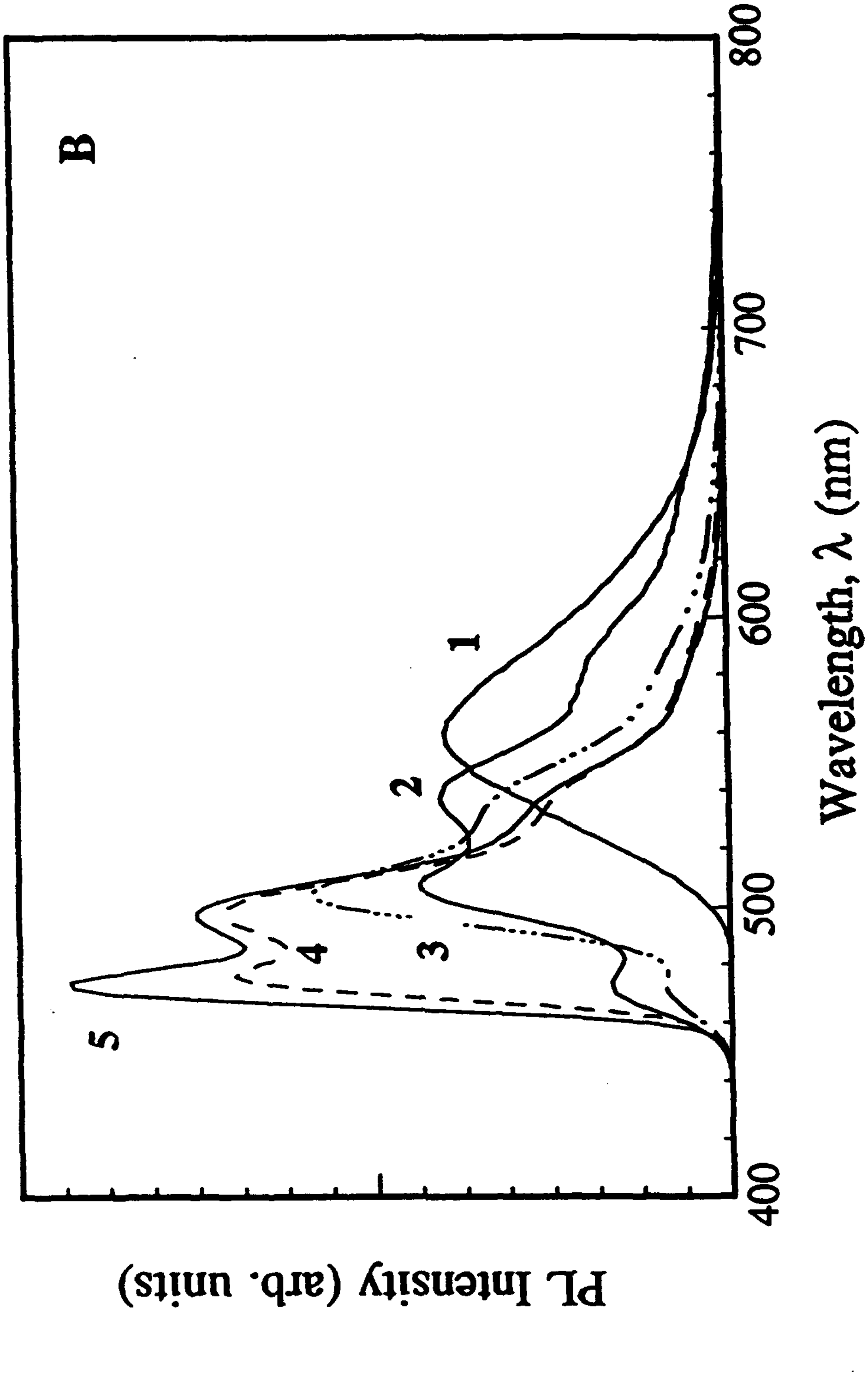

B
1
2
3
4
5
400
500
600
700
800
Wavelength, λ (nm)
PL Intensity (arb. units)

Fig. 3C

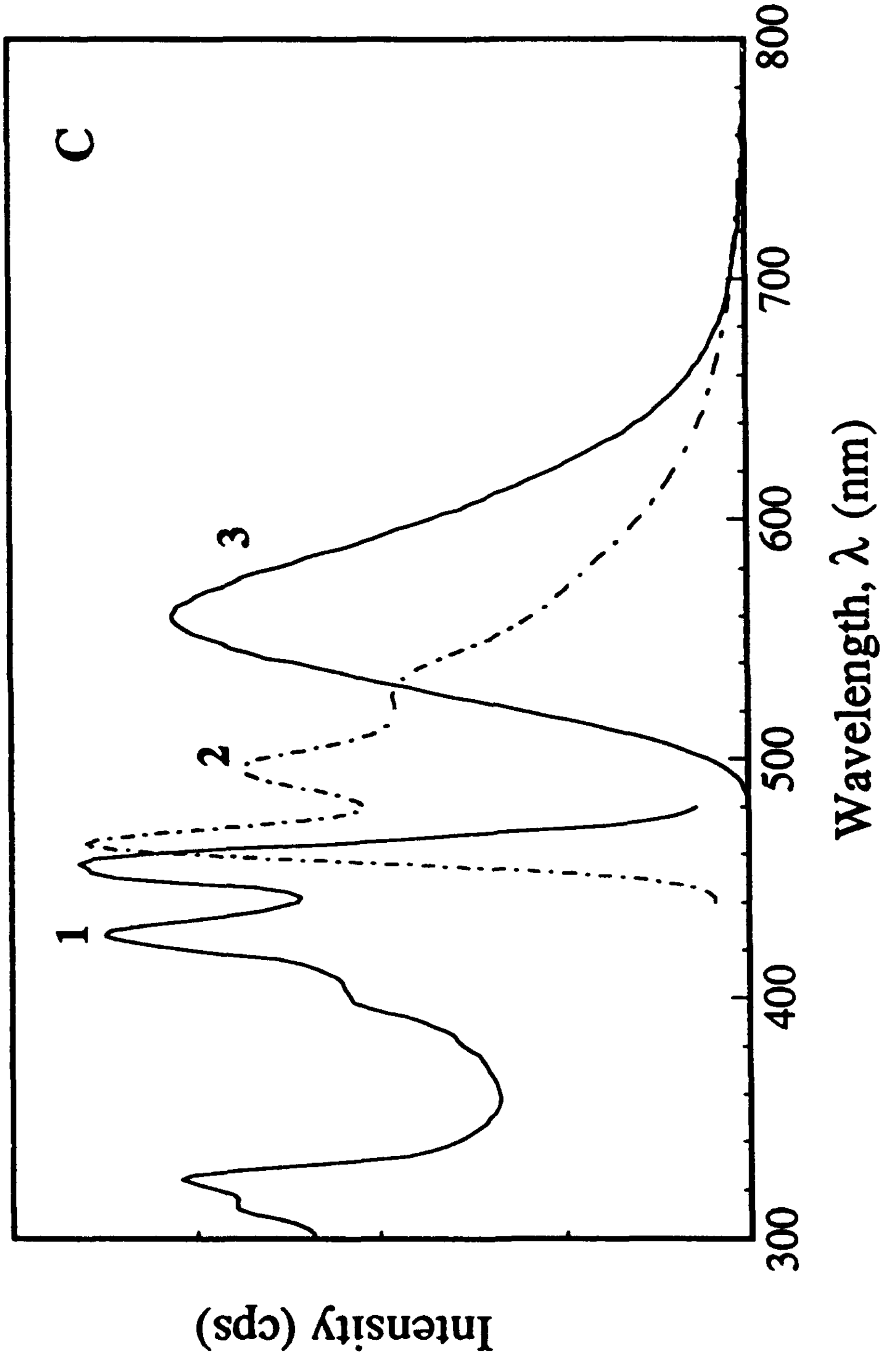


Fig. 4A

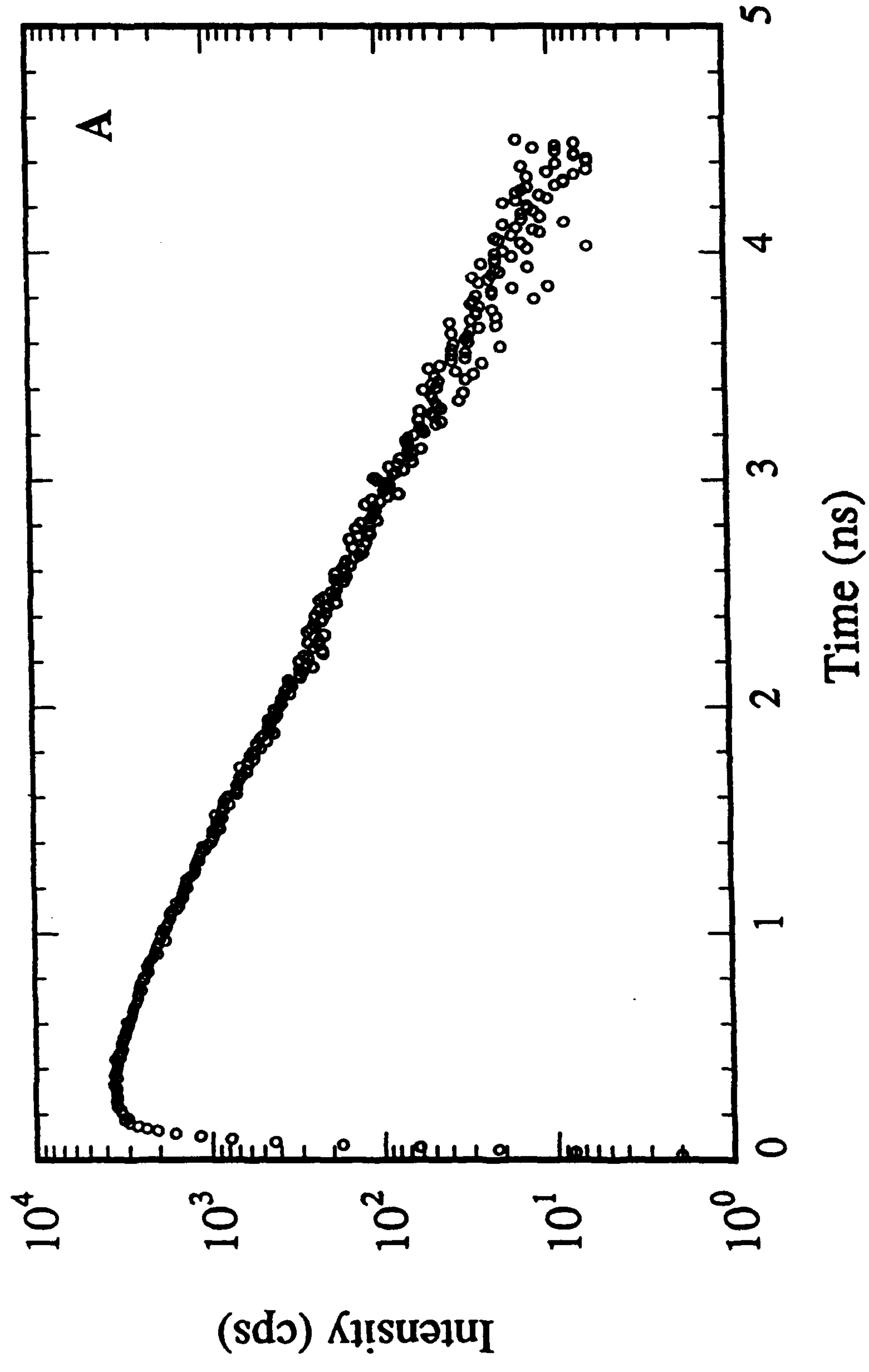


Fig. 4B

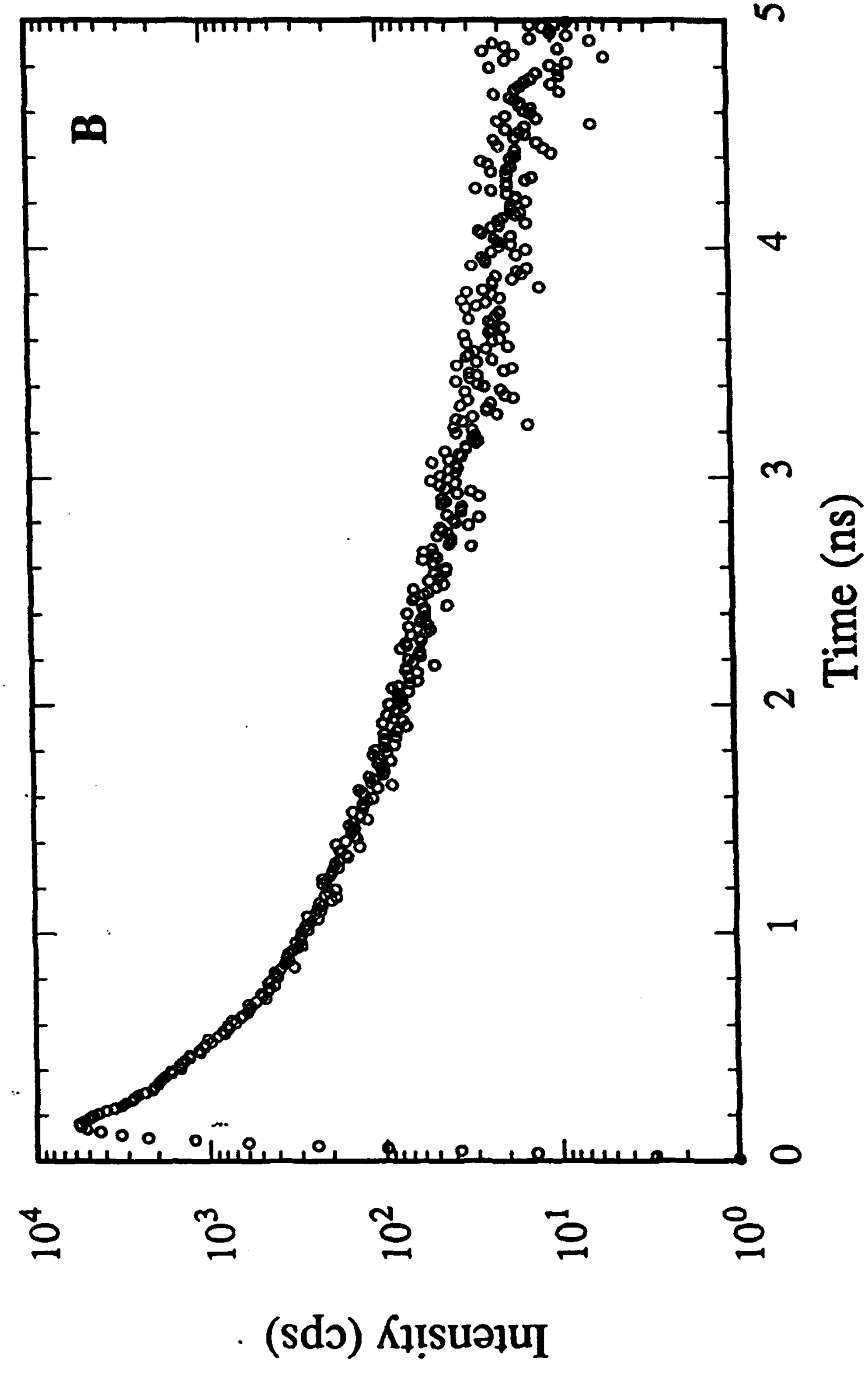


Fig. 5A

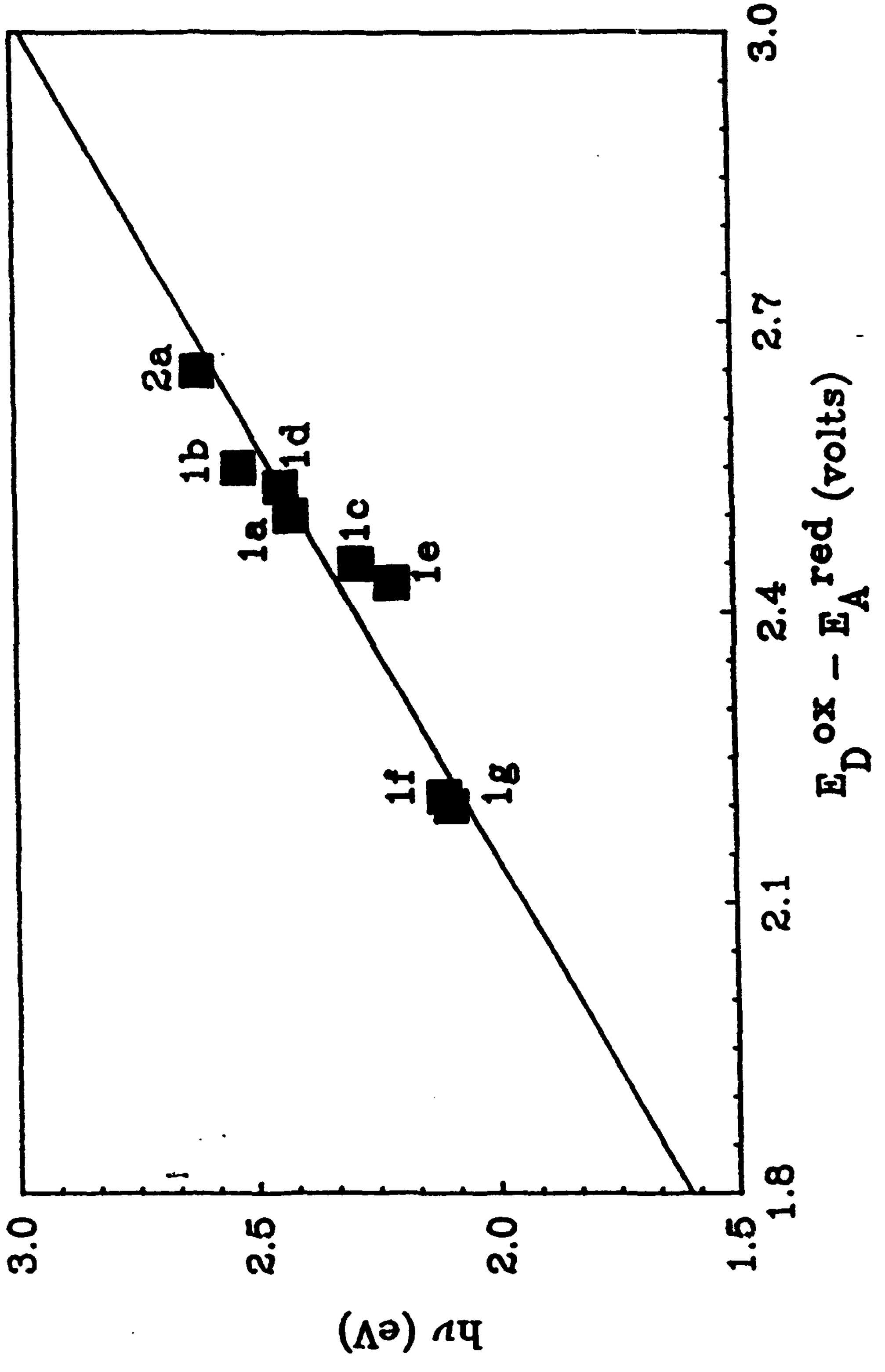

hν (eV)
3.0
2.5
2.0
1.5
1.8
2.1
2.4
2.7
3.0
$E_D^{ox} - E_A^{red}$ (volts)
2a
1b
1d
1a
1c
1e
1f
1g

Fig 5B