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Kenneth J. Wynne
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6. AUTHOR(S)
R. M. Tarkka and S. A. Jenekhe

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemical Engineering
University of Rochester
206 Gavett Hall
Rochester, NY 14627-0166

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13. ABSTRACT *(Maximum 200 words)*

Well known 2-(2-hydroxyphenyl)benzoxazole **1**, intramolecular hydrogen-bonded compound bis-2,5-(2-benzoxazolyl)phenol, **3**, and the new polymers poly(m-(2-hydroxy)-phenylene benzobisoxazole) (mHPBO, **4**) and poly(p-(2-hydroxy)-phenylene benzobisoxazole) (pHPBO, **5**), are used to elucidate the effects of molecular size, conjugation length, and competition with excimer formation on excited-state intramolecular proton transfer (ESIPT). It is shown that whereas **1**, **3** and **4** exhibit ESIPT, **5** does not. The results suggest that whereas molecular size does not appear to inhibit ESIPT, the competition with excimer formation and the extent of π-electron delocalization both do.

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Excited-State Intramolecualr Proton Transfer (ESIPT); ESIPT in polymers; photochromism; energy barrier; intramolecular hydrogen-bonded polymers; polybenzobisoxazole.

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Technical Report No. 10

Effects of Electronic Delocalization and Molecular Size on Intramolecular Proton Transfer

by

Richard M. Tarkka and Samson A. Jenekhe

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University of Rochester
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Rochester, NY

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Effects of Electronic Delocalization and Molecular Size on Intramolecular Proton Transfer

Richard M. Tarkka and Samson A. Jenekhe*

Department of Chemical Engineering and Center for Photoinduced Charge Transfer,
University of Rochester, Rochester, New York, 14627-0166

Abstract

Well known 2-(2-hydroxyphenyl)benzoxazole **1**, intramolecular hydrogen-bonded compound bis-2,5-(2-benzoxazolyl)phenol, **3**, and the new polymers poly(m-(2-hydroxy)-phenylene benzobisoxazole) (mHPBO, **4**) and poly(p-(2-hydroxy)-phenylene benzobisoxazole) (pHPBO, **5**), are used to elucidate the effects of molecular size, conjugation length, and competition with excimer formation on excited-state intramolecular proton transfer (ESIPT). It is shown that whereas **1**, **3** and **4** exhibit ESIPT, **5** does not. The results suggest that whereas molecular size does not appear to inhibit ESIPT, competition with excimer formation and the extent of π-electron delocalization both do.

Proton transfer reactions are ubiquitous. They are found in chemistry, biology, materials science, and other areas. The transfer of a hydrogen atom is the simplest of all atom transfer reactions and can be modeled by Marcus theory.[1] One special type of hydrogen atom transfer occurs intramolecularly upon photoexcitation. This excited state intramolecular proton transfer (ESIPT) process,[2,3] which was first described by Weller,[4] occurs generally in molecules in which an intramolecular hydrogen bond chelates an OH group to another heteroatom in the same molecule. The hydrogen atom transfer generally occurs very rapidly, even at 15K,[5] with time constants exceeding the ps time regime, and "without any *significant* barrier."[6] A population inversion of the keto tautomer results, and after the suggestion of Khan and Kasha[7], ESIPT processes have been employed for use as laser dyes, such as hydroxyflavone[8] in which the emission occurs at wavelengths significantly Stokes shifted (~100 nm) from the absorption. Photoinduced structural changes may also be the driving mechanism for new organic materials proposed for energy storage, data storage, and optical switching.[9] Other ways ESIPT processes are exploited include use as polymer photostabilizers[10,11] and triplet quenchers.[12]

Despite the relative simplicity of the hydrogen atom transfer reaction, and the interest in the use of the ESIPT processes in applications, the nature of the excited state potential energy surface is still unclear. Issues frequently investigated to help to ascertain the nature of the potential energy surface[2,3] include effect of solvent polarity and viscosity, hydrogen atom tunnelling, intersystem crossing to triplet states, the rate of reaction, and the existence and magnitude of an energy barrier between enol and keto states.

Our recent interest includes the photochemistry and photophysics of conjugated polymers.[13] Excimers and exciplexes have been observed in polymers such as poly(p-phenylene benzobisoxazole) (PBO), **2**.[13a] The similarity in structure of 2-(2-hydroxyphenyl)benzoxazole, **1**, in which ESIPT has been well documented,[11,14,15,16] to the rigid-rod polymer **2** has prompted us to begin investigation of ESIPT in macromolecules. We have adopted the central theme of the interaction between structure and reactivity to assess the importance of molecular size, extended conjugation, and competition with excimer formation on the ESIPT potential energy surface. To date, there has been only one report claiming an ESIPT process to occur in a macromolecule,[17] though the validity of this claim is uncertain since the possibily of a competitive excimer formation pathway, which would lead to similar observations, was not ruled out.

In this paper, intramolecular hydrogen-bonded compounds **1**, **3**, **4** and **5** are used to explore the effects of molecular size, conjugation length, and competition with excimer formation on ESIPT. UV-Vis, steady state fluoresence and picosecond time-resolved photoluminesence (PL) decay measurements are reported for the new polymers **4** and **5**, in both pristine form and in thin solid films of poly (methyl methacrylate) (PMMA), as well as for the model compounds **1** and **3** in thin solid films of PMMA.

Model compound **1** was supplied by Aldrich. Compound **3** was prepared by the condensation of 2-hydroxyterephthalic acid[18] with 2-aminophenol (Aldrich).[19] Polymers **4** and **5** were prepared by condensation of 4,6-diamino-1,3-benzenediol (DABDO) with 4-hydroxyisophthalic acid (Aldrich) and 2-hydroxyterephthalic acid respectively, as described elsewhere.[20] 4,6-dinitro-1,3-benzenediol[21] was reduced to DABDO with Sn/HCl in EtOH/H_2O,[22] and was then precipitated as its dihydrochloride salt in 10 M HCl. DABDO was recrystallized from 3M HCl prior to use. Compounds **3**, **4** and **5** were characterized by NMR, IR and UV/Vis spectroscopies and found to be consistent with the proposed structures.[23]

Thin solid films of **4** and **5** in both pristine state and in PMMA, and model compounds **1** and **3** in PMMA were spin coated onto silica from their solutions in nitromethane/$GaCl_3$ as described previously.[24] Techniques and instrumentation used to obtain optical absorption and steady state photoluminesence (PL) spectra, and picosecond time-resolved PL decay measurements (time-correlated single-photon-counting technique) are as described elsewhere.[13b,25]

UV-Vis and fluoresence spectra, and time-resolved fluoresence decay kinetics were determined for model compound **1** in thin solid films of PMMA at 0.01, 0.1, 1 and 10 weight % respectively (Figure 1). The steady-state emission has no concentration dependence with the single emission band in all cases appearing at 492 nm, which is strongly Stokes shifted from the absorption maximum of 324 nm in accord with previous solution studies.[11,14,15,16] The time resolved PL decay (inset, Figure 1) also shows no concentration dependence. The decay in all cases is biexponential with components of 1.2 ns and 4.2 ns, with amplitudes of 18 % and 82 %, respectively.

Features of the photophysical data of **3** (not shown) indicate that this compound also exhibits the expected ESIPT: no concentration dependence of the energy or shape of emission band; large Stokes shift (500 nm emission *vs.* 370 nm absorption), and concentration independent decay of the emission band with time constants of 1.0 ns and 3.0 ns with amplitudes of 10 % and 90 %, respectively.

Figure 2 shows the steady-state flouresence emission spectra of thin films of **4** in its pristine form and in thin solid films of PMMA at 0.5 and 0.005 weight % respectively. No concentration dependence of the band shape or energy is apparent. The major emission band appears in all cases with a maximum value at 503 nm, which is strongly Stokes shifted from the absorption maximum of 360 nm. A shoulder is also seen in all cases with maximum value at 450 nm. The time resolved PL decay of the 503 nm emission band of the pristine polymer **4** shows that the emitting species decays very quickly, with the dominant component having a lifetime on the order of 50 ps. Upon dilution in thin solid films of PMMA, however, the decay slows significantly with the emission kinetics having concentration independent biexponential time constants of 1.1 and 3.1 ns (amplitudes of 22 % and 74 % respectively) which compares well with the results obtained for **1**.

The very fast decay (~50 ps) and large Stokes shift of the 503 nm band in the pristine film of **4** is consistent with excimer decay, which we have observed in several rigid-rod polymers.[13a] Upon dilution in PMMA to block the excimer pathway, however, the emission band does not shift to higher energies, as is usually the case when the excimer formation pathway is blocked. The relatively long wavelength of the emission band in these dilute thin solid films must arise from an ESIPT pathway, since the excimer pathway is blocked. The possibility that excimer formation and ESIPT pathways occur simultaneously in pristine **4** and have coincident emission wavelength cannot be ruled out. However, the fast decay of the emitting species indicates that excimer formation is at least as competitive as the ESIPT pathway and consequently that the barrier to excimer formation is at least as small as that for ESIPT. This barrier is small enough though that when the excimer path is blocked, ESIPT can occur.

The emission spectra of **5** (Figure 3) differ markedly from that of **4** and the model compounds **1** and **3**. A thin film of pristine **5** exhibits a featureless emission band with a maximum at 492 nm, which is blue shifted by 13 nm compared to **4**, despite a 67 nm red shift in the absorption band. Additionally the emission maximum exhibits a blue shift with decreasing concentration in PMMA. At 2×10^{-3} weight % in PMMA, the emission band shows fine structure with a very small Stokes shift. This data is almost identical to that obtained for the unsubstituted polymer **2**,[23,26] which has been attributed to excimer emission from the pristine film which yields to "regular" singlet emission (small Stokes shift) when the excimer pathway is blocked. The time-resolved fluoresence decay kinetics of the emission band of **5** also shows a concentration dependence in PMMA. The decay is much faster than for **4**; the time constants of 0.2 ns and 0.9 ns (which vary in amplitude with concentration in PMMA) are markedly different from that of polymer **4**. Taken together, the data clearly indicates that excimer formation alone occurs in the pristine film of **5**. Upon dilution in PMMA, the emission band shifts to higher energy as excimer formation gives way to emission from the enol form. There is an energy barrier to ESIPT which cannot be overcome in the case of **5**.

Several factors can be ruled out as the source of the large energy barrier to ESIPT in **5**. Molecular size cannot be the source of the barrier since this would require **4** to be void of ESIPT. Effects of the PMMA host can be ruled out since **1**, **3** and **4** all exhibit ESIPT in PMMA. Excimer formation, which does inhibit ESIPT in the pristine polymers, is blocked in the PMMA films and is not competitive. One possible source of the barrier to ESIPT is the extended conjugation of the *para* -linked **5** compared to the *meta* linked **4**. If **1**, **3** and **4** are considered, which all exhibit ESIPT, it is seen that the absorption band of the enol form is much more sensitive to conjugation effects than the emission band of the keto tautomers. Whereas the absorption maximum ranges from 324 nm to 370 nm, the variation in the emission band is significantly smaller (492-503 nm). It is likely that the energy level of the excited state enol form is most sensitive to perturbation and decreases in energy relative to the energies of the ground state enol form and both the excited and ground state energies of the keto form. The result of this is that on the excited state energy surface, the enol energy is lowered relative to the keto energy, which will induce an increase in the energy barrier between the two states in accord with Hammond's postulate.[27] In the case of the highly conjugated **5**, the energy barrier is sufficiently high to inhibit ESIPT.

In conclusion, we have investigated the effects of conjugation, molecular size and competition with excimer formation on the potential energy surface for ESIPT in hydroxyphenyl benzoxazole compounds. Molecular size was found to have little if any effect on ESIPT. Excimer formation was found to occur preferentially over ESIPT in both of the pristine polymers studied, implying the existence of at least a small energy barrier to ESIPT in both polymers. In the case of the *para* -linked **5**, extended conjugation leads to a sufficently large energy barrier that ESIPT is not observed. When the conjugation is reduced by linking the polymers *meta*, as in **4**, the barrier is sufficiently reduced that ESIPT occurs. Further studies of ESIPT in macromolecules are presently being conducted.

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References and Notes.

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1. Marcus, R.A. *J. Am. Chem. Soc.* **1969**, *91*, 7224-7225.

2. Barbara, P.F.; Walsh, P.K.; Brus, L.E. *J. Phys. Chem.* **1989**, *93*, 29-34.

3. See the special issue: *Chem. Phys.* **1989**, *136*, 153-360.

4. Weller, A. *Z. Elektrochem.* **1956**, *60*, 1144-1147.

5. Dick, B. *Chem. Phys. Lett.* **1989**, *158,* 37-44.

6. Ernsting, N.P., Mordzinski, A.; Dick, B. *J. Phys. Chem.* **1987**, *91*, 1404-1407.

7. Khan, A.U.; Kasha, M. *Proc. Natl. Acad. Sci. USA.* **1983**, *80*, 1767-1770.

8. Brucker, G.A.; Swinney, T.C.; Kelley, D.F. *J. Phys. Chem.* **1991**, *95*, 3190-3195.

9. Nishiya, T.; Yamauchi, S.; Hirota, N.; Baba, M.; Hanazaki, I. *J. Phys. Chem.* **1986**, *90*, 5730-5735.

10. Heller, H.J.; Blattmann, H.R. *Pure Appl. Chem.* **1973**, *36*, 141-161.

11. Williams, D.L.; Heller, A. *J. Phys. Chem.* **1970**, *74*, 4473-4480.

12. Werner, T. *J. Phys. Chem.* **1979**, *83*, 320-325.

13 (a). Jenekhe, S.A.; Osaheni, J.A. *Science.* **1994**, *265*, 765-768.
(b). Osaheni, J.A.; Jenekhe, S.A. *J. Am. Chem. Soc.* **1995**, in press.

14. Woolfe, G.J.; Melzig, M.; Schneider, S.; Dorr, F. *Chem. Phys.* **1983**, *77*, 213-221.

15. Rodriguez-Preito, M.F.; Nickel, B.; Grellman, K.H.; Mordzinski, A. *Chem. Phys. Lett.* **1988**, *146*, 567-569.

16. Itoh, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1561-1565.

17. Hammond, D.R.; Mehta, P.G.; Takiff, L. *Chem. Mater.* in press.

18. Miura, Y.; Torres, E.; Panetta, C.A. *J. Org. Chem.* **1988**, *53*, 439-440.

19. Mordzinski, A.; Grabowska, A.; Kuhnle, W.; Krowczynski, A. *Chem. Phys. Lett.* **1983**, *101*, 291-296.

20. Osaheni, J.A.; Jenekhe, S.A. *Chem. Mater.* **1992**, *4*, 1282-1290.

21. Schmitt, R.J; Ross, D.S.; Hardee, J.R.; Wolfe, J.F. *J. Org. Chem.* **1988**, *53*, 5568-5569.

22. Doxsee, K.M.; Feigel, M.; Stewart, K.D.; Canary, J.W.; Knobler, C.B.; Cram, D.J. *J. Am. Chem. Soc.* **1987**, *109*, 3098-3107.

23. Tarkka, R.M.; Jenekhe, S.A., unpublished results.

24. Jenekhe, S.A.; Johnson, P.O.; Agrawal, A.K. *Macromolecules*, **1989**, *22*, 3216-3222.

25. Jenekhe, S.A.; Osaheni, J.A. *Chem. Mater.* **1994**, *6*, 1906-1909.

26. Osaheni, J.A.; Jenekhe, S.A. *Macromolecules*, **1994**, *27*, 739-742.

27. Hammond, G.S. *J. Am. Chem. Soc.* **1955**, *77*, 334-338.

Figure Captions.

Figure 1. Optical absorption spectrum of 2-(2-hydroxyphenyl)benzoxazole, **1,** 1 weight % in a thin solid film of PMMA(dashed curve); photoluminesence spectra ($\lambda_{\text{excitation}}$ = 380 nm) of **1** in PMMA at 10 %, 1 %, 0.1 %, and 0.01 % (solid curves).

INSET: Time-resolved PL decay dynamics of **1** in PMMA at 10 %, 1 %, 0.1 %, and 0.01 % ($\lambda_{\text{emission}}$ = 490 nm).

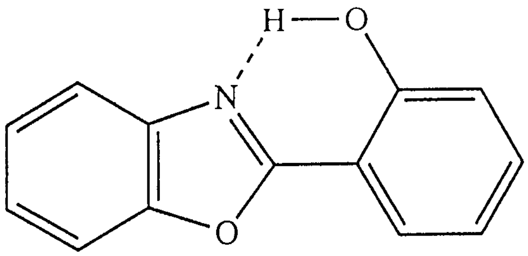
Figure 2. Optical absorption spectrum of a thin film of mHPBO, **4,** ······· ; photoluminesence spectra ($\lambda_{\text{excitation}}$ = 350 nm) of **4**: pristine film — — — ; 0.5 weight % in PMMA —— ;

4 x 10^{-2} weight % in PMMA —·—·— ;

INSET: Time-resolved PL decay dynamics of **4**: Pristine film, $\lambda_{\text{emission}}$ = 500 nm (Curve A); 0.5 weight % in PMMA, $\lambda_{\text{emission}}$ = 500 nm (Curve B); 5 x 10^{-3} weight % in PMMA , $\lambda_{\text{emission}}$ = 500 nm (Curve C).

Figure 3. Optical absorption spectrum of a thin film of pHPBO, **5,** ······; photoluminesence spectra ($\lambda_{\text{excitation}}$ = 380 nm) of **5**: pristine film ——; 0.5 weight % in PMMA —·—; 5 x 10^{-3} weight % in PMMA — — — .

INSET: Time-resolved PL decay dynamics of **5**: Pristine film, $\lambda_{\text{emission}}$ = 490 nm (Curve A); 0.5 weight % in PMMA, $\lambda_{\text{emission}}$ = 490 nm (Curve B); 5 x 10^{-3} weight % in PMMA , $\lambda_{\text{emission}}$ = 440 nm (Curve C)



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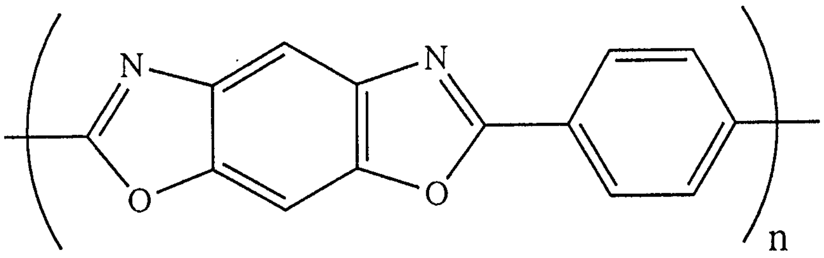

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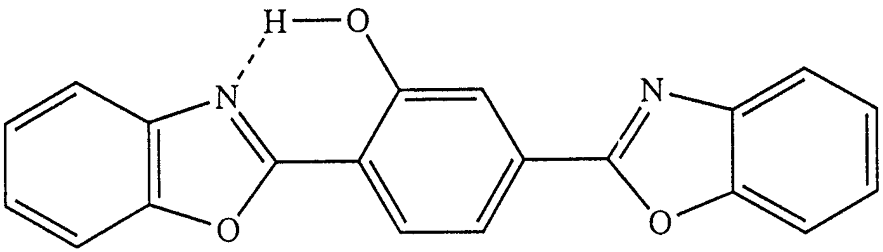

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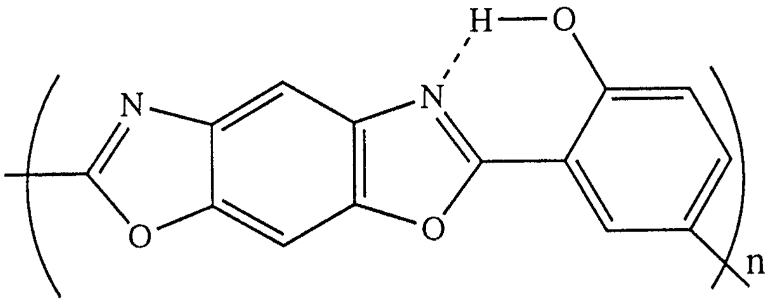

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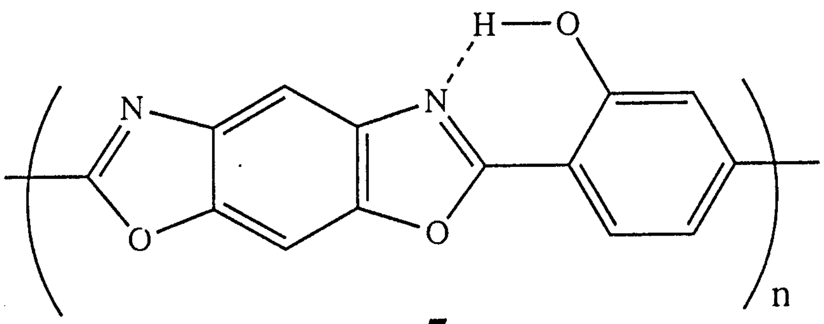

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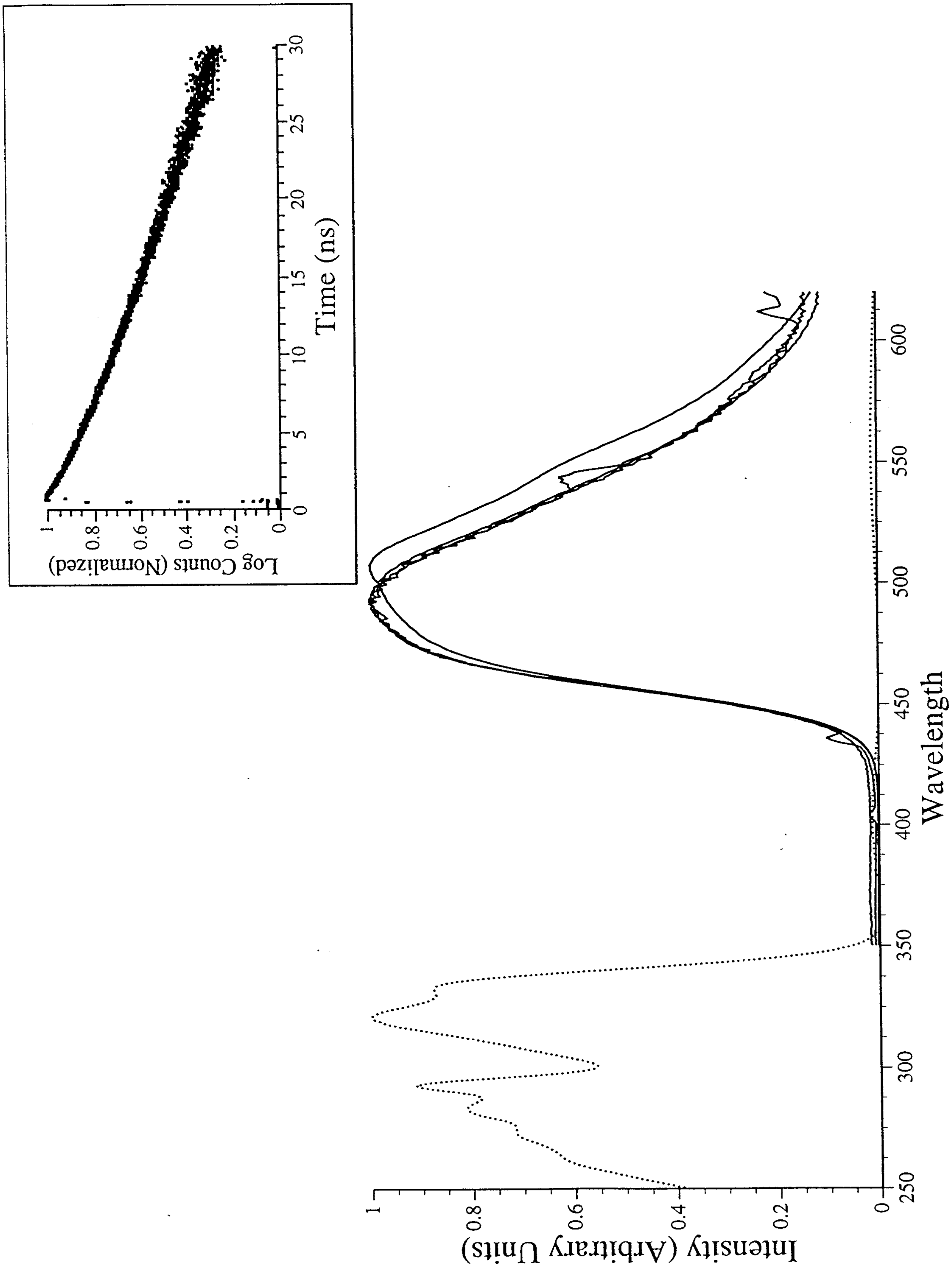
FIG 1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400
450
500
550
600
Wavelength
Log Counts (Normalized)
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0.4
0.6
0.8
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0
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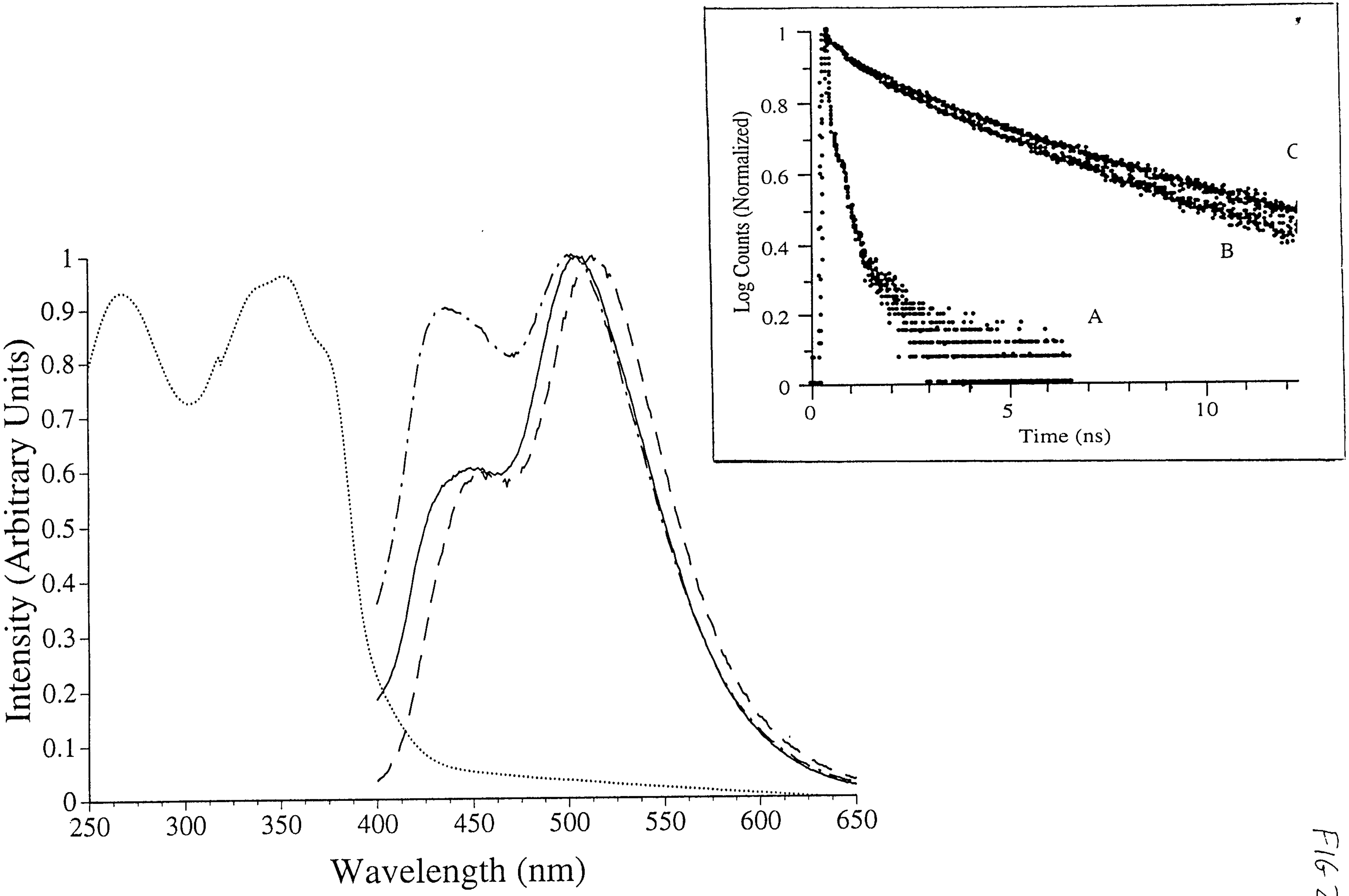
10
15
20
25
30
Time (ns)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350
400
450
500
550
600
650
Wavelength (nm)
Log Counts (Normalized)
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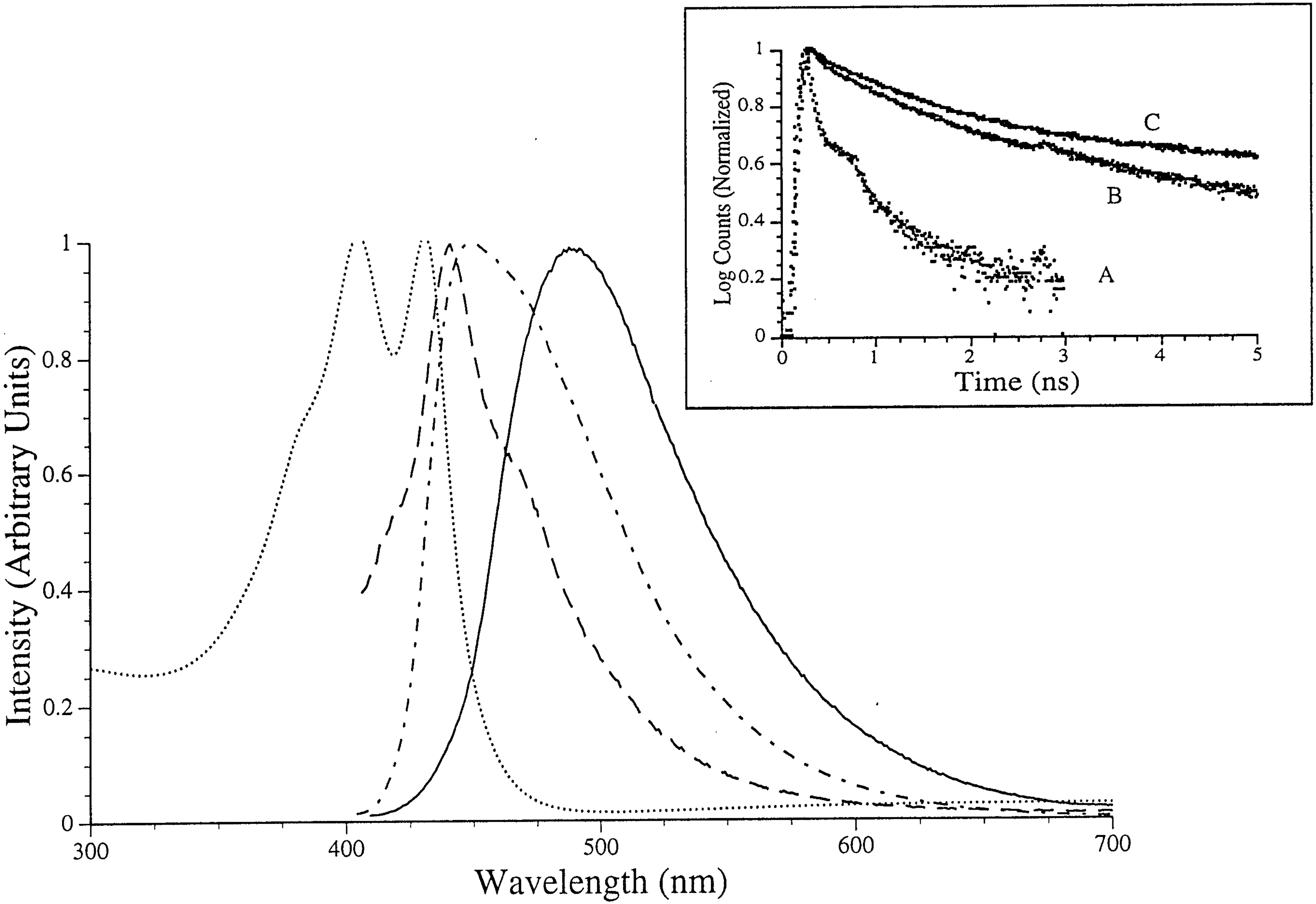
10
Time (ns)
A
B
C

FIG 2

FIG 3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Log Counts (Normalized)
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0.4
0.6
0.8
1
0
1
2
3
4
5
Time (ns)
A
B
C

Effects of Electronic Delocalization and Molecular Size on Intramolecular Proton Transfer

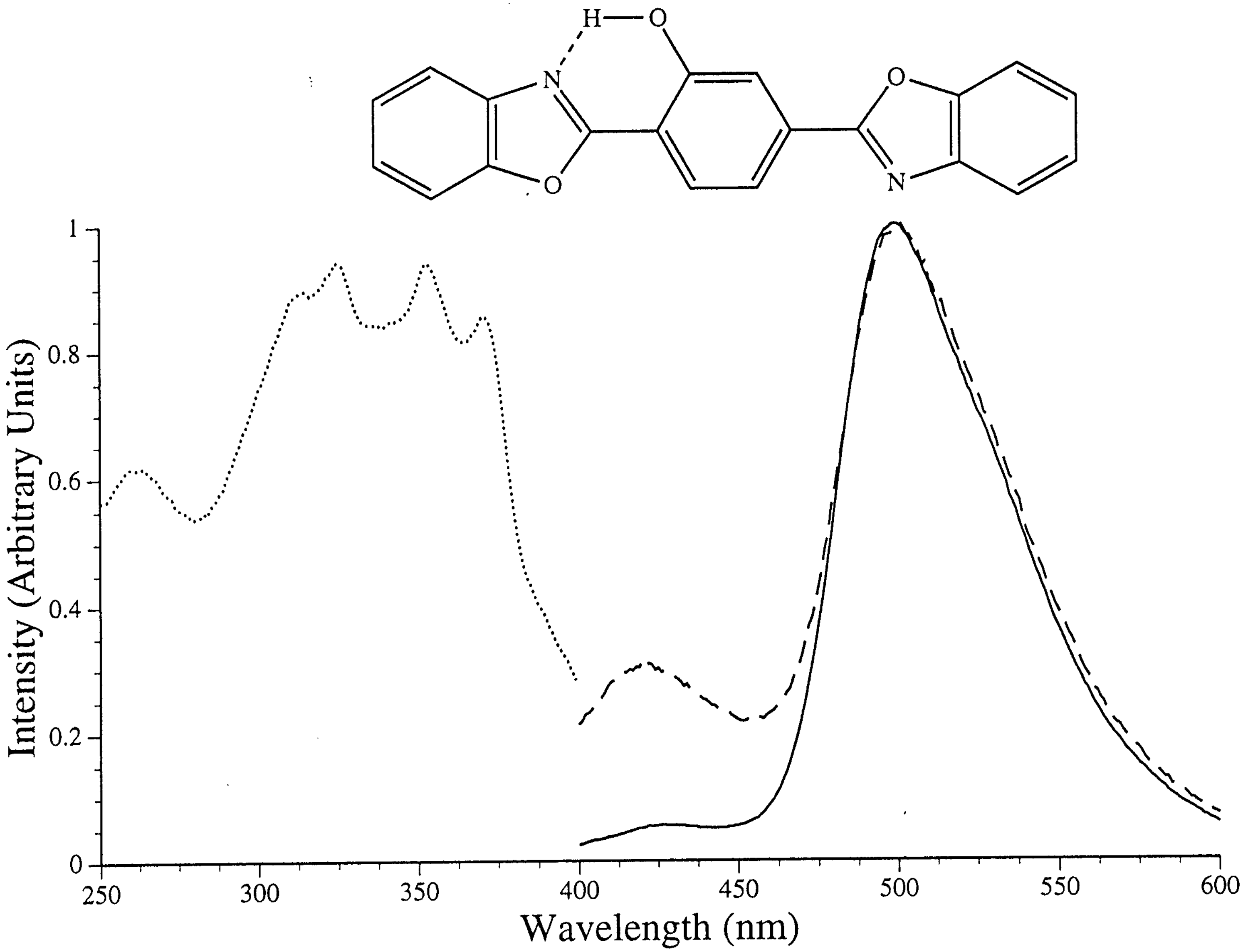
Richard M. Tarkka and Samson A. Jenekhe*

Department of Chemical Engineering and Center for Photoinduced Charge Transfer,
University of Rochester, Rochester, New York, 14627-0166

SUPPLEMENTARY MATERIAL

Figure S1. Optical absorption spectrum of bis-2,5-(2-benzoxazolyl)phenol in a thin solid film of PMMA, 1.0 weight % .... ; Photoluminesence spectra ($\lambda_{excitation}$ = 350 nm) of **3** in PMMA: 1.0 weight % ———— 10^{-2} weight %. —— —— ——

Figure S2: Time-resolved photoluminesence decay dynamics of **3** dissolved in thin solid films of PMMA (1.0 and 10^{-2} weight %, respectively). ($\lambda_{emission}$ = 490 nm)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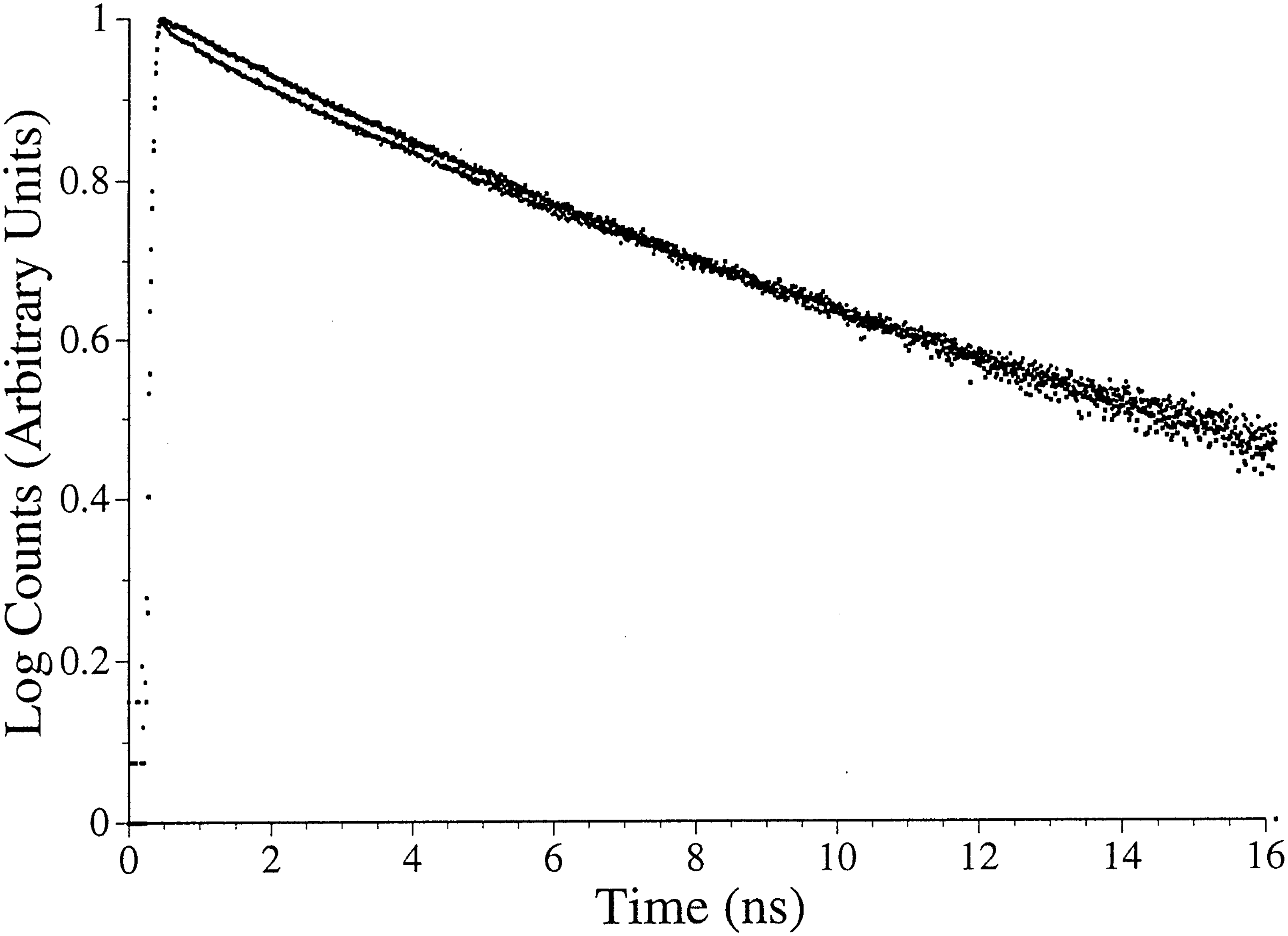
Wavelength (nm)

Fig S2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