

108] Wei-Szu Chang, Ting-Hua Li, **Shun-Chi Chen**(陳順基), "Exciplex Formation and Charge-Transfer Induced Photoreduction of Excited 2-Benzoylfluorene with Triethylamine", 2010 APCCChE (13th Asia Pacific Confederation of Chemical Engineering Congress), Taipei, Taiwan, Oct. 5-8, 2010.

[109] Guang-Rong Zeng, Tzu-Chiang Lin, **Shun-Chi Chen**

Dear Dr. Chen and Dr. Fang:

A friend gave me a e-copy of your publication ([CPL 450 \(2007\) 65-70](#) which I find interesting to me. Similarly, I would be interested to see other pertinent articles on the subject, including the one cited above. If you have information related on the absorptions of PBP and chiefly BF in different solvents (e.g., spectra or absorptivities/extinction coefficients at given maxima in benzene, dry/or wet acetonitrile, dimethylformamide, methanol, absolute/or wet ethanol, and halocarbons) and still other data about the excited states, radicals and radical-ions I would much appreciate if you would make me available via e-reprint, e-mail or in print to michaeltot@hotmai.com (or tothms@live.com) or to Michael Toth, 45 Myrtle St. Apt. 21, Boston, MA 02114-4559.

During the early and mid seventies, I investigated photoreactions of benzophenone, the much studied so called self-quenching included, and benzil in CFC's and other solvents, etc.. Thus the determination of spectra and absorptivities for triplets and radicals came up. The method of simple ground state depletion appears to be applicable to the very high intensity ruby laser photolysis of PBP in acetonitrile but not in benzene. The same method is well applicable to the high intensity photolysis of BF in varied solvents (see [Toth Mihaly, Chem. Phys. 46 \(1980\) 437-443](#)). Also, I tried to photo stabilize strongly irradiated dilute solutions by triplet energy transfer and by electron transfer in selected polar solvents (e.g. dry acetonitrile, water, dimethylformamide) Indeed, I have found that the chemically reversible photo reduction by DABCO via free radical-ions is a versatile reaction in the just cited solvents. Of course eventually used information coming from your works, after your permission, would be acknowledged.

Unfortunately, at this time of working on publications, I do not have access to academic journals at universities or on the internet, unless I would pay about \$ 40.00 per article, without even knowing what is in it. I have difficulty to afford the fast internet.

I will greatly appreciate your attention, sincerely, Michael Toth

PS, sorry in the earlier e-mail, I have misspelled the address of Dr.Fang

Observation of A Novel Emission from An Exciplex of
Triplet 4-Phenylbenzophenone with Triethylamine

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Abstract:

Exciplex formation of excited 4-phenylbenzophenone (PBP) triplet with triethylamine (TEA) in organic solution has been studied by steady state and pulse-laser photoluminescence measurements. Direct evidence for triplet exciplex formation was provided by the observation of emission at longer wavelengths than that of the phosphorescence of PBP. Some other interesting features which have been attributed to the lowest excited triplet state of the PBP molecule of the exciplex were also observed. The quenching mechanism is proposed to involve a π, π^* triplet of PBP to form an exciplex with the ground state of TEA. The critical border difference of the photophysics between $^3(\pi, \pi^*)$ PBP and $^3(n, \pi^*)$ benzophenone (BP) probably plays an important role in electron-transfer process.

Keywords: Triplet exciplex emission; 4-phenylbenzophenone phosphorescence; Triethylamine



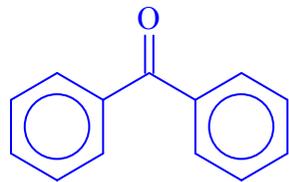
4-苯基二苯甲酮與三乙胺電荷-轉移誘導 激態複合體的形成及其光化學的應用

**The Exciplex Formation of Charge-Transfer Induced 4-
Phenylbenzophenone with Triethylamine and the Application in
Photochemistry**

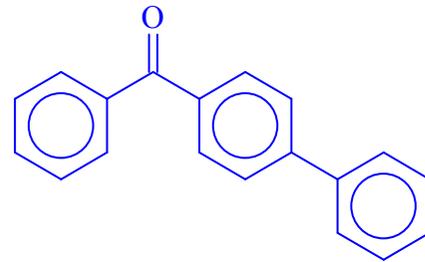
研究生：陳順基
指導教授：方泰山博士

摘要(一)

本論文為研究4-苯基二苯甲酮 (PBP) 在凝相中的光物理性質，並與二苯甲酮 (BP) 作比較，探討其最低激發參態組態對其光物理及光化學的影響。研究結果證實 PBP 的最低激發單、參態分別為 $S_1(n, \pi^*)$ 及 $T_1(\pi, \pi^*)$ ，因此一個分子內的能量轉移由羰基的 $n \rightarrow \pi^*$ 轉移到連苯的 $\pi^* \rightarrow \pi$ ，激發區域則落在“連苯+羰基”上。



Benzophenone (BP)



4-Phenylbenzophenone (PBP)

摘要(二)

使用穩態及脈衝-雷射光激發光，研究激發參態 PBP 的磷光強度及生命期被三乙基胺 (TEA) 的分子間淬熄。參態激態複合體 (triplet exciplex) 形成的直接證據為觀察到比 PBP 磷光的更長波長的發光。因此，提出 PBP 參態淬熄的機構，為包含著與基態 TEA 形成的激態複合體中間體，並導致激態複合體的發光。

摘要(三)

溶劑極性在激態複合體動力學上一些效應，可解釋介於激態複合體間的電荷-轉移交互作用。不同供電子能力的胺類之淬熄速率常數與胺類的游離能有關，這趨勢也反映在PBP與各種胺類（例如二乙基胺、二丙基胺、三乙基胺、三丙基胺及三異丙基胺）激態複合體形成的活化能。

2010 APCChE (13th Asia Pacific Confederation of Chemical Engineering Congress), Taipei, Taiwan, Oct. 5-8, 2010.

The 13th Asia Pacific Confederation of
Chemical Engineering Congress

APCChE 2010
October 5-8, 2010, Taipei

Exciplex Formation of Excited 2-Benzoylfluorene with Triethylamine

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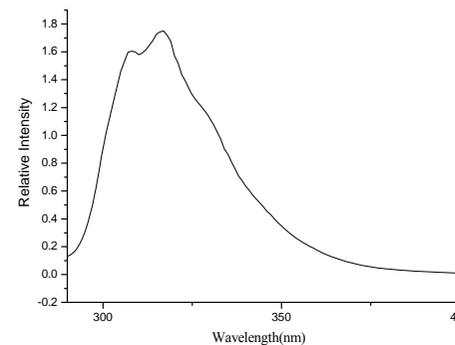
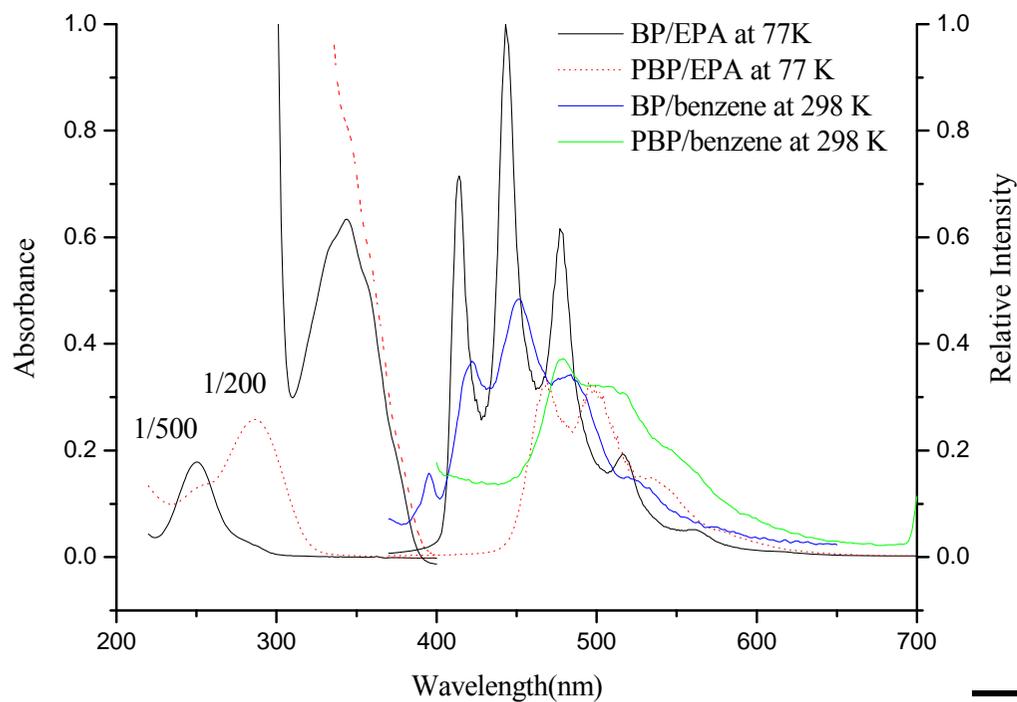
*E-mail: scchen@mail.mcut.edu.tw

Keywords: 2-Benzoylfluorene; Photophysics; Solvent effect.

Abstract

Synthesis of 2-benzoylfluorene (BF), and compare its photophysical and photochemical behaviors with 4-benzoylbiphenyl (BB) in organic condensed phase. The absorption and emission spectra of BF were measured in various solvents. The emission of BF and BB quenching by triethylamine (TEA) have been studied in benzene using steady state and pulse-laser photoluminescence techniques. The results show that both BF and BB can form exciplexes with TEA at room temperature. It has been found that the photoexcitation proceeds to rapid charge transfer to form the exciplex. The BF-TEA exciplex emission peak located at 640 nm and had a lifetime of about 9 μ s. The Stern-Volmer quenching constant of BF is smaller than that of BB. By comparing the molecular structures and energy levels of BF and BB, it is demonstrated that the photophysical properties has an effect on the exciplex formation.

PBP的光物理



BP及PBP在EPA溶劑中的吸收光譜、77 K低溫磷光光譜以及
在苯溶劑中常溫degas發光光譜

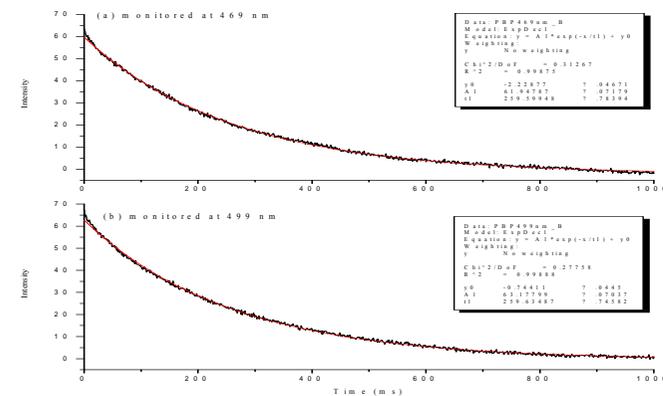
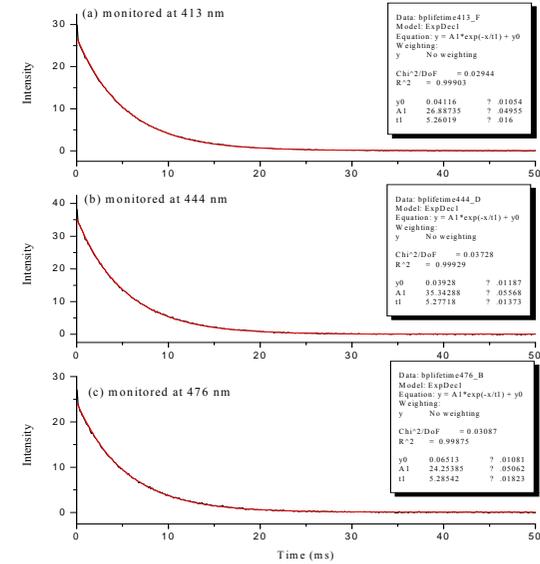
BP及PBP螢、磷光相對量子產率

化合物名稱	298 K		77 K	
	Φ_f	Φ_p	Φ_f	Φ_p
BP	~ 0	1.5×10^{-3}	~ 0	0.72
PBP	~ 0	9.5×10^{-4}	~ 0	0.46
BF		1.4×10^{-4}	~ 0	0.13

PBP的光物理

BP及PBP在EPA中的低温磷光生命期

Monitored at	τ_p	R^2
BP (413 nm)	5.26 ms	0.9990
BP (444 nm)	5.28 ms	0.9993
BP (476 nm)	5.29 ms	0.9988
PBP (469 nm)	259.6 ms	0.9987
PBP (499 nm)	259.6 ms	0.9989



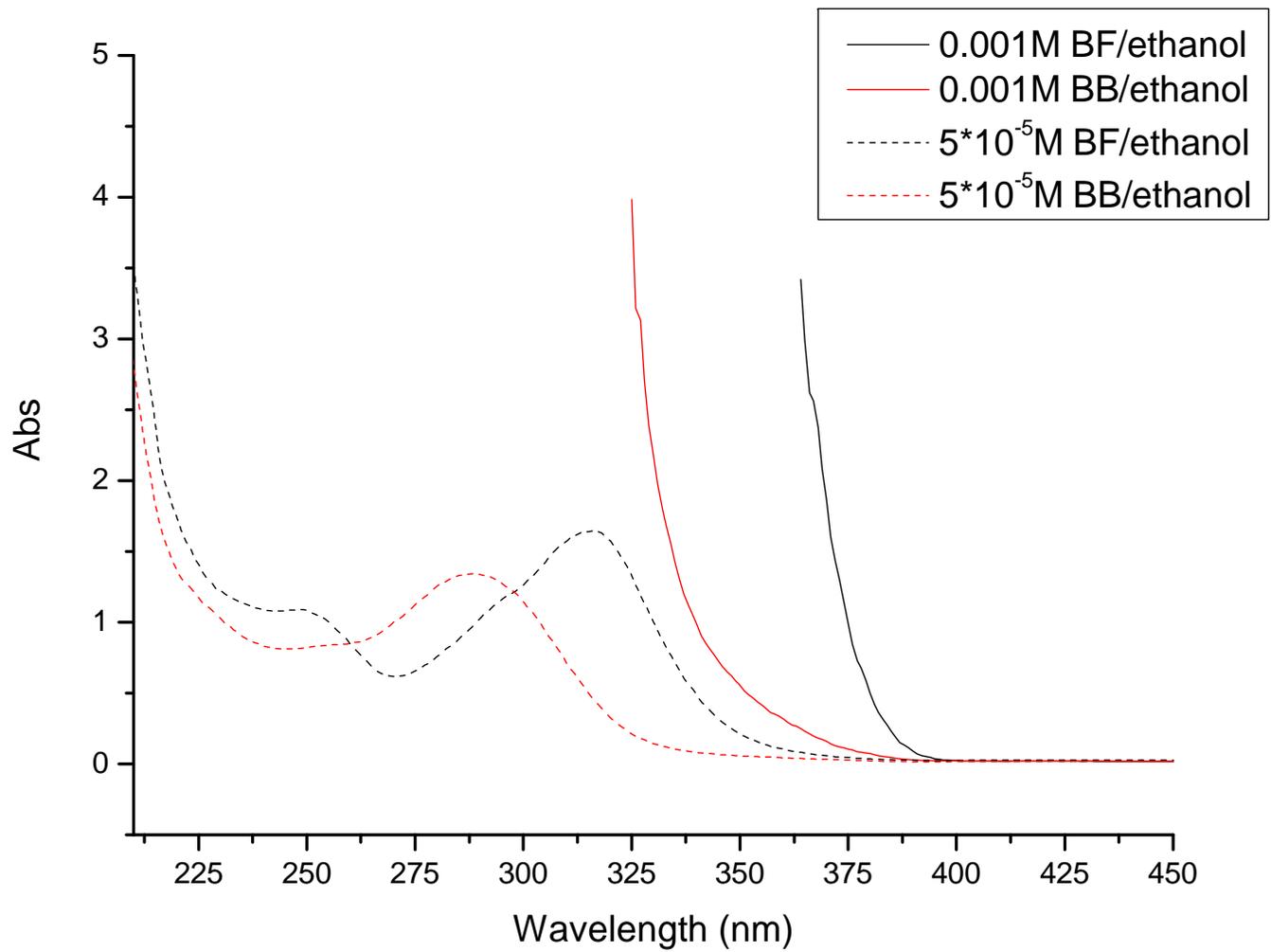


Figure 1 : Absorption spectra of **BF** and **BB** in ethanol solvent.

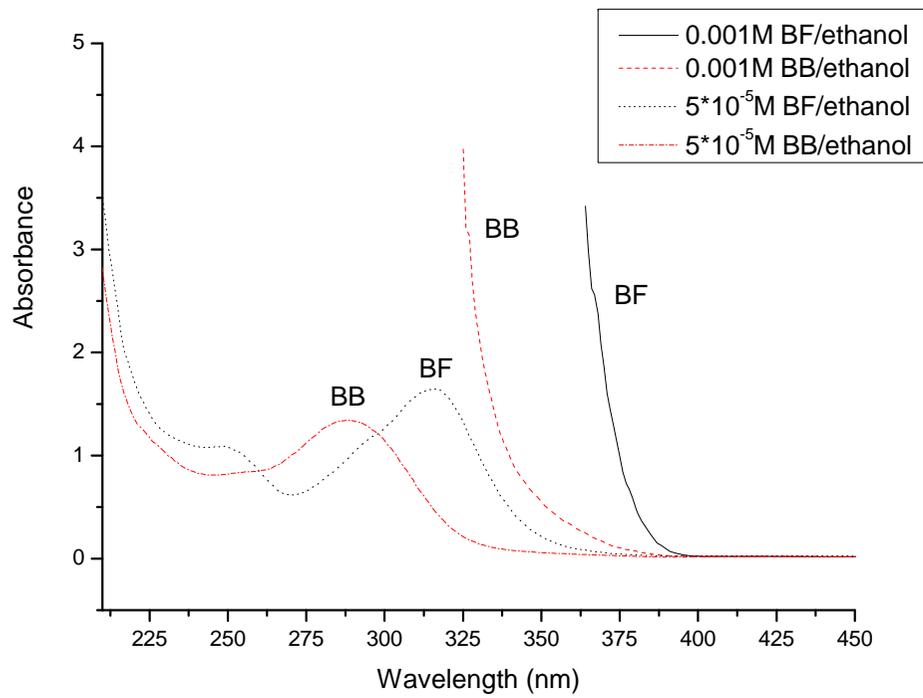


圖4-9： 5×10^{-5} M (左半部)和 1×10^{-3} M (右半部)的2-苯甲醯萸(BF)與4-苯甲醯聯苯(BB)在乙醇中的吸收光譜圖

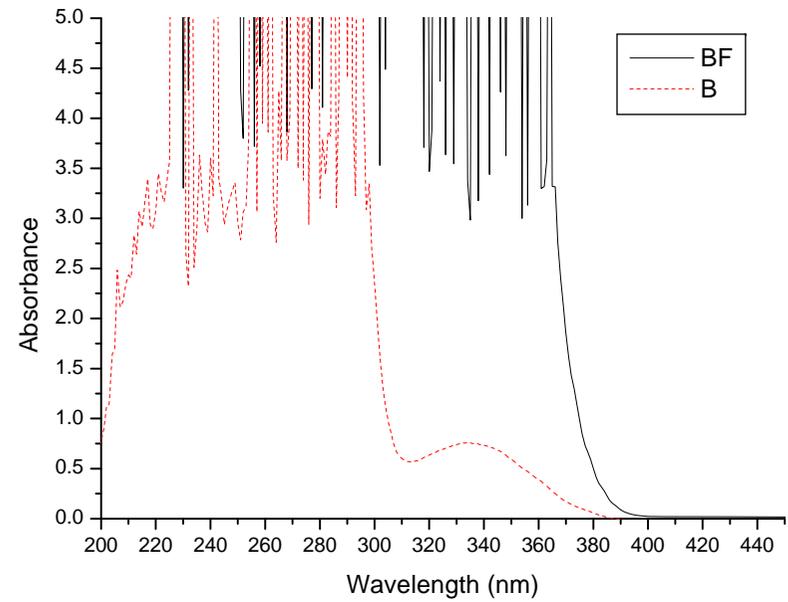


圖4-10： 5×10^{-3} M的2-苯甲醯萸(BF)與苯甲醯萸(B)在乙醇中的吸收光譜

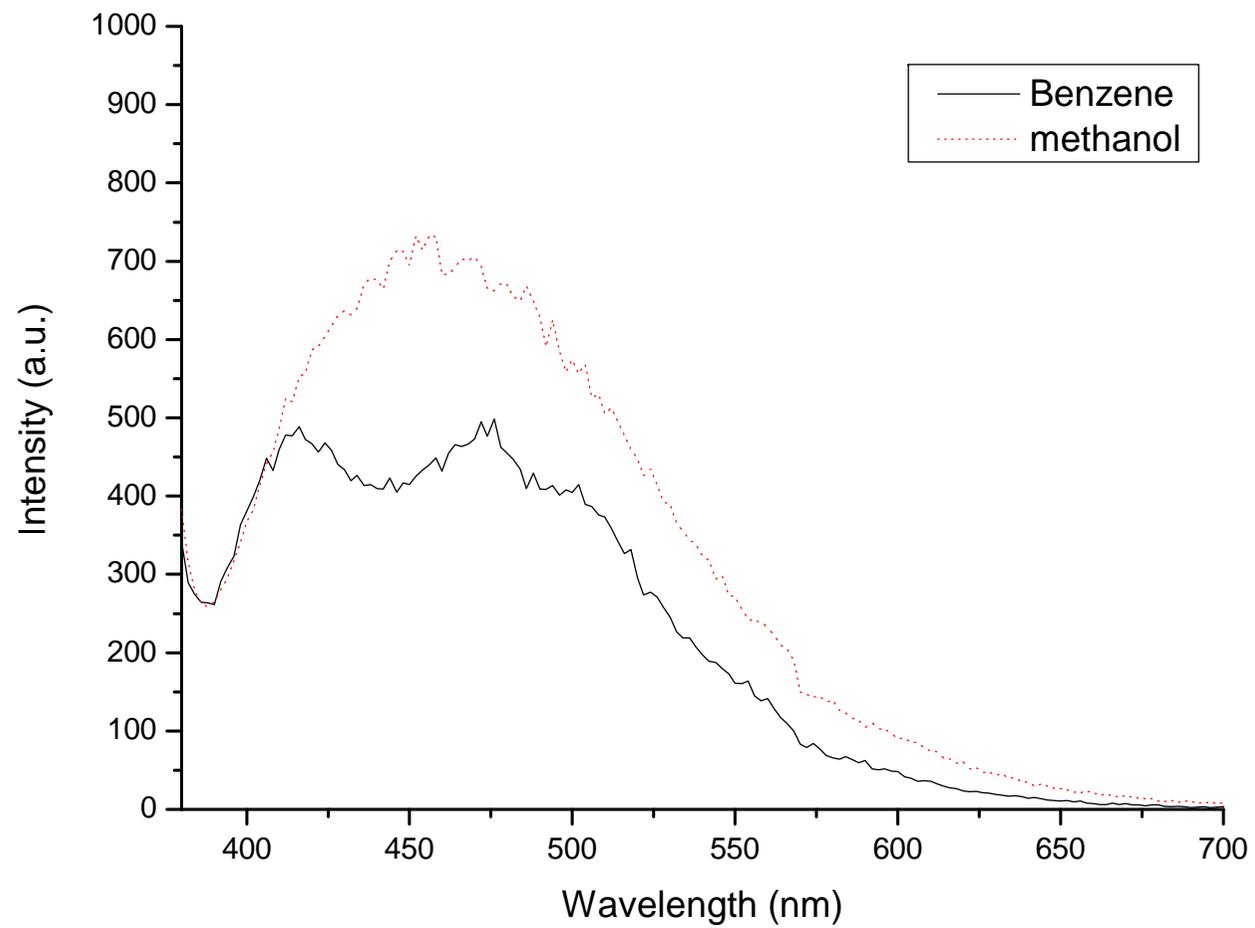


圖4-11： 5×10^{-3} M的BF在不同溶劑中的發光光譜(激發波長為360 nm)

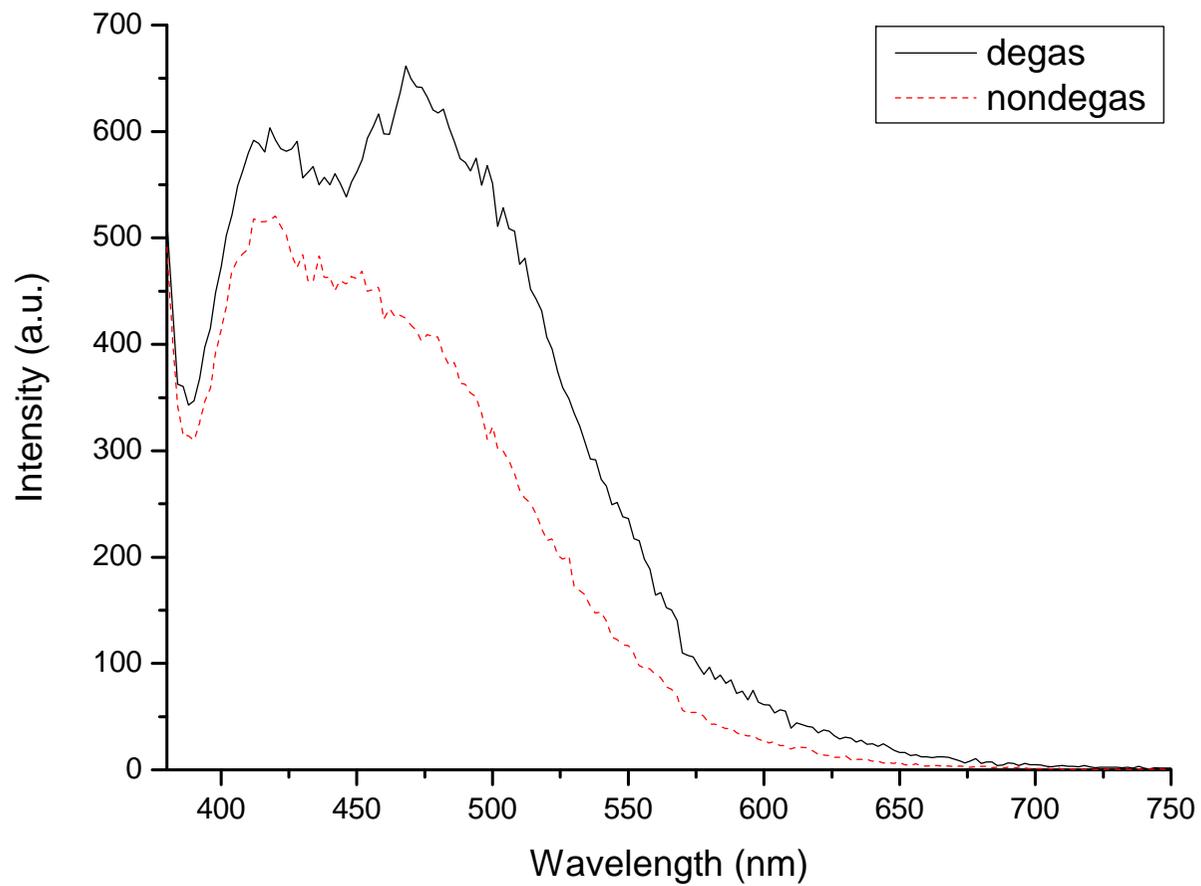


圖4-12： $5 \times 10^{-3} \text{ M}$ BF在苯溶劑中的degas和nondegas發光光譜圖(激發波長為360nm)

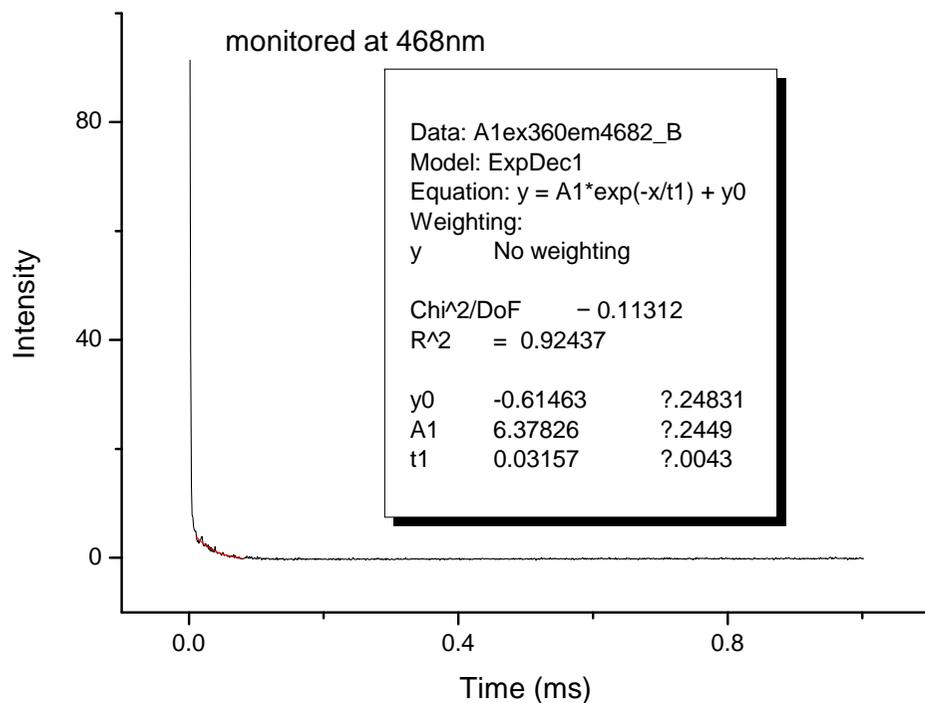


圖4-13： 5×10^{-3} M BF在苯溶劑中的degas磷光生命期(Delay time 0.001 ms, Gate time 0.001 ms, Ex wavelength 360nm, Em wavelength 468nm)

圖4-13為BF室溫下的磷光生命期，其生命期經計算後約有 $32 \mu\text{s}$ ，比較文獻⁽¹⁸⁾中B的室溫磷光生命期只有 $6 \mu\text{s}$ ，在相同濃度下，BF磷光生命期明顯大於B，這代表著BF的磷光是屬於 (π, π^*) 躍遷。

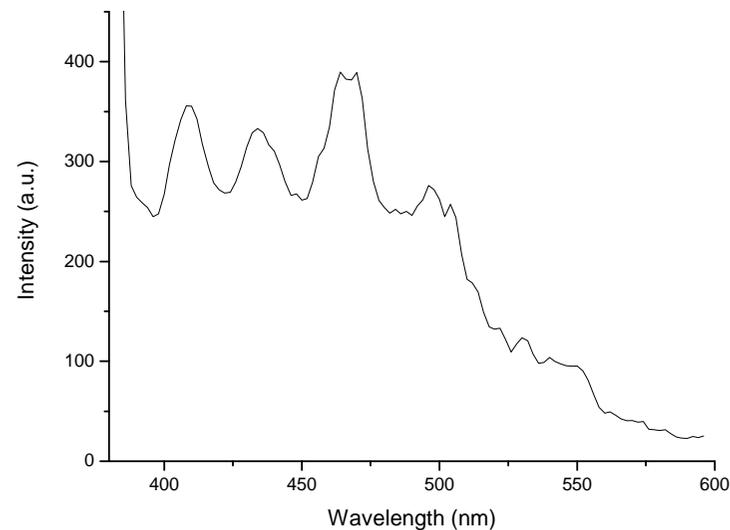


圖4-14： 5×10^{-3} M BF在EPA溶劑中的低溫發光光譜(激發波長為360 nm)

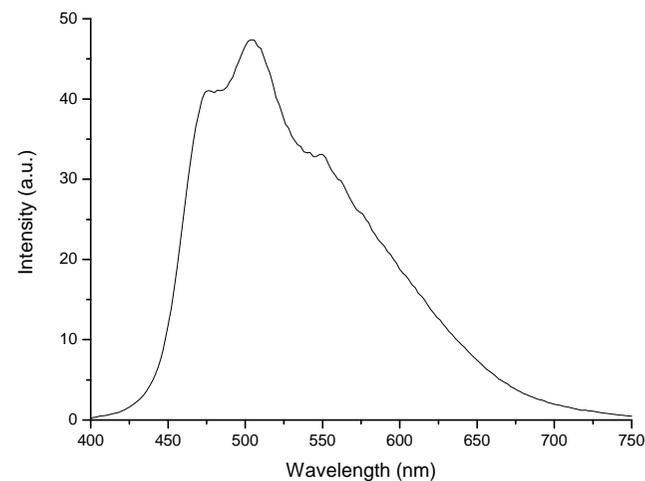


圖4-15： 5×10^{-3} M BF在苯溶劑中的時間分離光譜(delay time 0.1 ms)

表4-3：B與BF的磷光相對量子產率
化合物B之數據參考文獻⁽⁵³⁾

化合物名稱	298 K	77 K
	Φ_p	Φ_p
B	1.5×10^{-3}	0.72
BF	1.4×10^{-4}	0.13

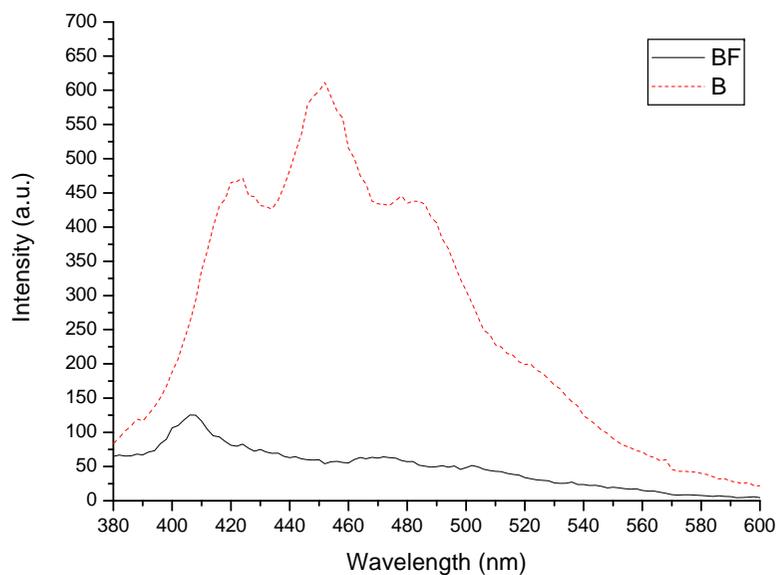


圖4-17： 1×10^{-3} M BF與 5×10^{-3} M B
在苯溶劑中degas的室溫發光光譜
(O. D. matched at 360 nm)

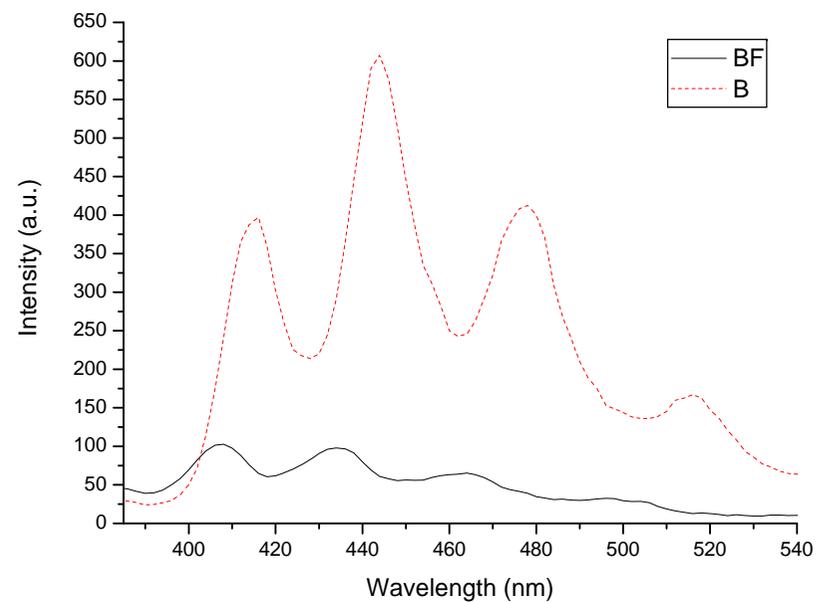


圖4-18： 5×10^{-4} M BF與 5×10^{-3} M B在EPA溶劑中的低溫
發光光譜
(O. D. matched at 357 nm)

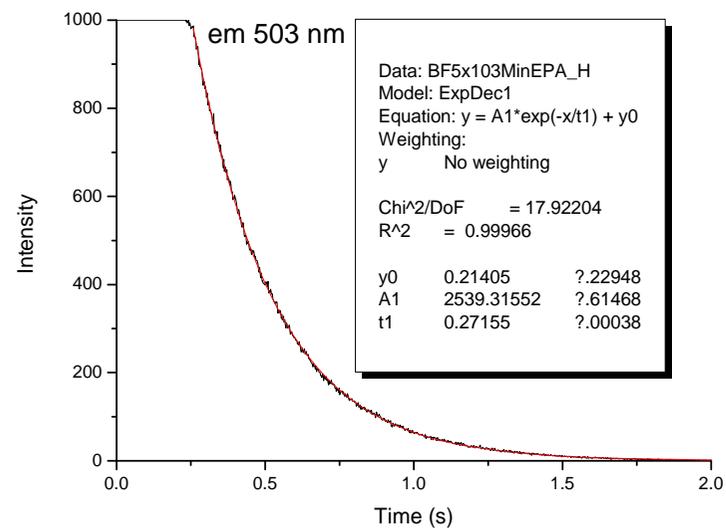
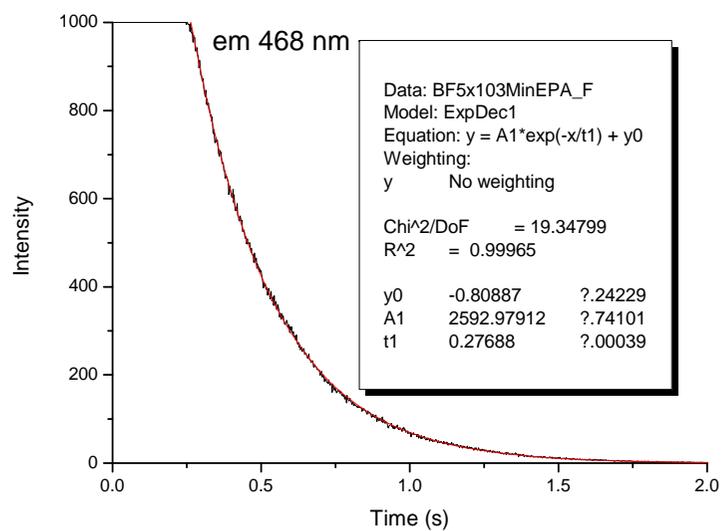


圖4-16： 5×10^{-3} M BF在EPA溶劑中的低溫生命期(Delay time 1 ms, Gate time 2 ms, Ex wavelength 360 nm)

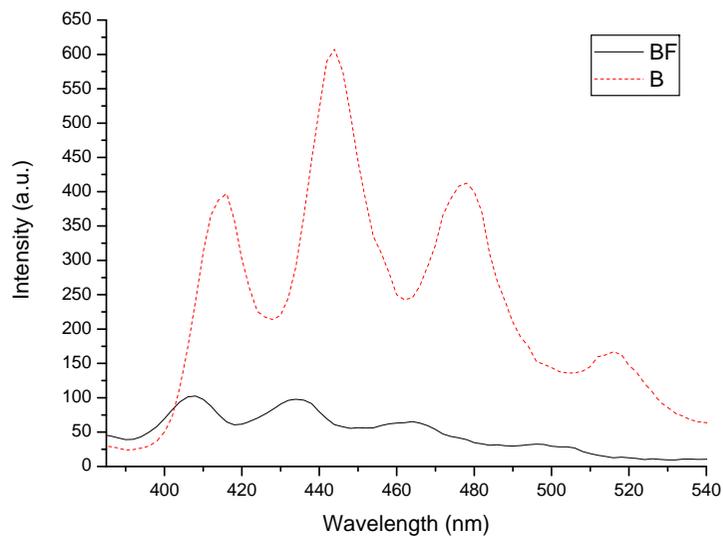


圖4-18： 5×10^{-4} M BF與 5×10^{-3} M B在EPA溶劑中的低溫發光光譜
(O. D. matched at 357 nm)

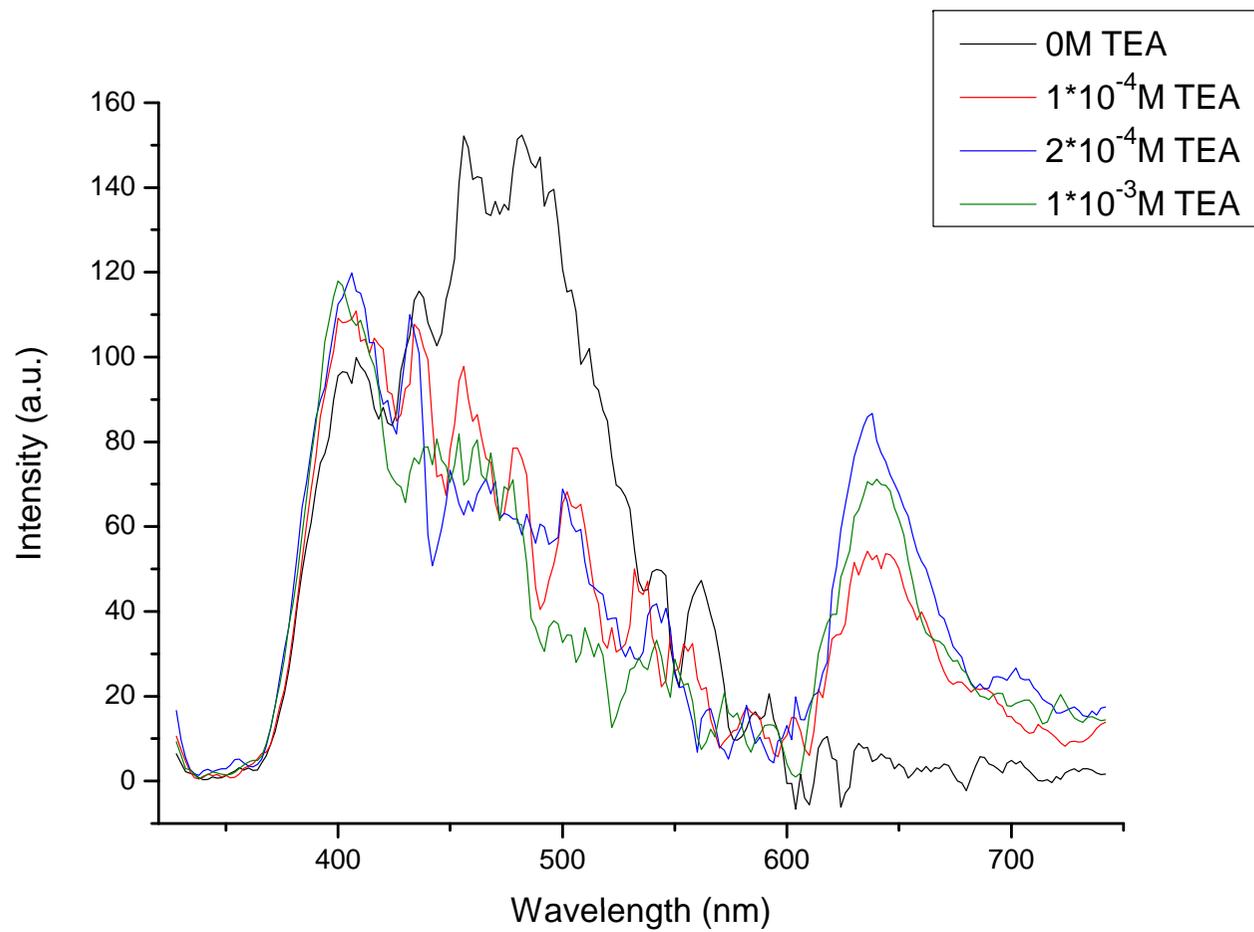
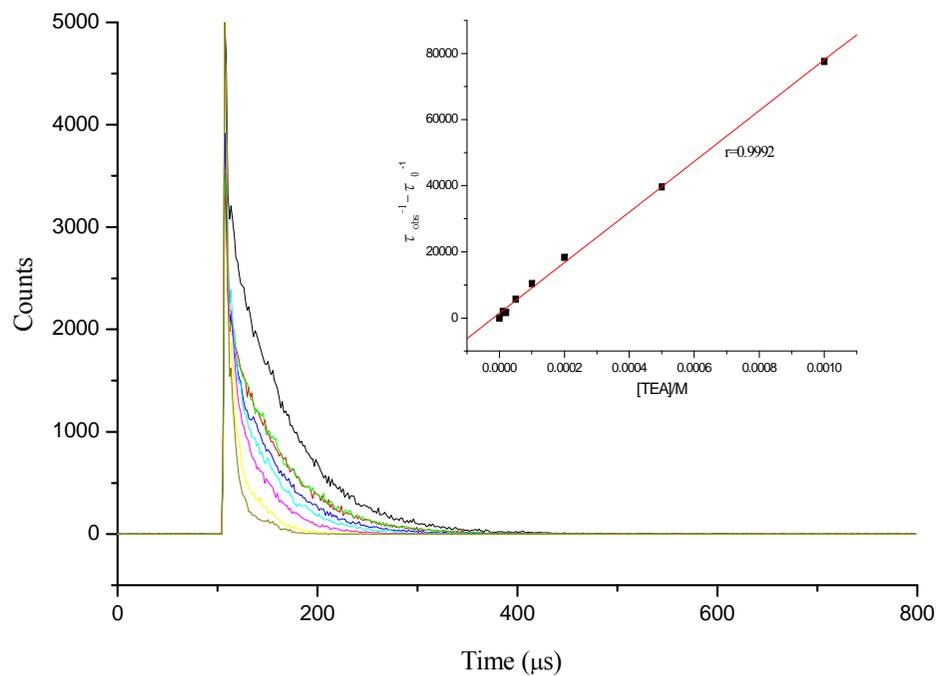


Figure 2 : Emission quenching of degassed 5×10^{-3} M BF in benzene by various concentrations of TEA.

TEA淬熄PBP (BF)的磷光生命期(in benzene)



TEA的濃度 (M)	PBP(BF)的生命期 ^a (μs)
0	41.4 (31.57)
1×10^{-5}	39.5 (21.24)
2×10^{-5}	39.7
5×10^{-5}	36.3 (20.58)
1×10^{-4}	33.0
2×10^{-4}	28.6
5×10^{-4}	21.0
1×10^{-3} ($2-5 \times 10^{-3}$)	14.3 (11.36—5.76)

$$k_q = 4.52 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$

$$(k_q = 2.6 \times 10^7 \text{ M}^{-1}\text{s}^{-1})$$

a. Monitored at 480nm

References

1. Chen S.-C., and Fang T.-S. Charge-transfer induced photoreduction of 4-phenylbenzophenone by triethylamine and the application in photopolymerization, *Chemistry (The Chinese Chem. Soc., Taipei)*, **66(3)**, 1-8, 2008.
2. Chen S.-C., and Fang T.-S. Observation of a novel emission from an exciplex of triplet 4-phenylbenzophenone with triethylamine, *Chem. Phys. Lett.*, **450**, 65–70, 2007.
3. Frederichs B., and Staerk H. Energy splitting between triplet and singlet exciplex states determined with E-type delayed fluorescence *Chem. Phys. Lett.*, **460**, 116–118, 2008.
4. Cho D. W., Fujitsuka M., Yoon U. C., and Majima T. Intermolecular exciplex formation and photoinduced electron transfer of 1,8-naphthalimide dyads in methylated benzenes *Journal of Photochemistry and Photobiology A: Chemistry* **190**, 101–109, 2007.
5. Choudhury S. D., Basu S. Singlet state exciplex formation of phenazine with some aromatic amines, *Chem. Phys. Lett.*, **373**, 67-71, 2003.
6. Kawai A., Noguchi S., and Obi K. Competition between exciplex formation and hydrogen abstraction reaction in benzophenone/1,4-cyclohexadiene binary clusters, *Chem. Phys. Lett.*, **362**, 397–402, 2002.
7. Yatsunami T., Nakajima Y., Shimada T., and Inoue H. Photophysical Properties of Intramolecular Charge-Transfer Excited Singlet State of Aminofluorenone Derivatives, *J. Phys. Chem. A*, **102**, 3018-3024, 1998.

**PROTOTROPIC REACTIONS OF 2-CARBONYLSUBSTITUTED
FLUORENES IN THE GROUND AND
FIRST EXCITED SINGLET STATES**

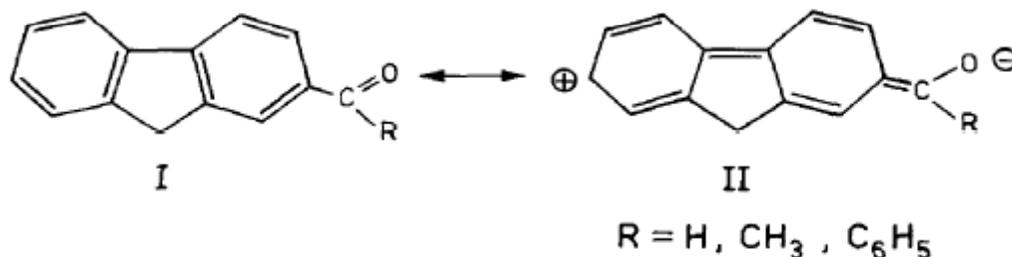
RAMASAMY MANOHARAN and SNEH K. DOGRAT

Department of Chemistry, Indian Institute of Technology, Kanpur-208016 (India)

(Received April 7, 1989; in revised form June 26, 1989)

Summary

The spectral characteristics of 2-fluorenaldehyde, 2-acetylfluorene and 2-benzoylfluorene have been studied in different solvents and at various acid concentrations. This study has shown that $n\pi^*$ may be the lowest energy transition in non-polar and aprotic solvents but that OTT^* is the lowest energy transition in water. The carbonyl group attains more planarity with respect to the fluorene moiety on excitation. The prototropic equilibrium follows the benzophenone acidity scale rather than Hammett's acidity scale. A medium effect is also observed during the protonation of the species. Contrary to literature reports at $H, -8$ the dication species are formed by protonating the ca



Scheme 1.

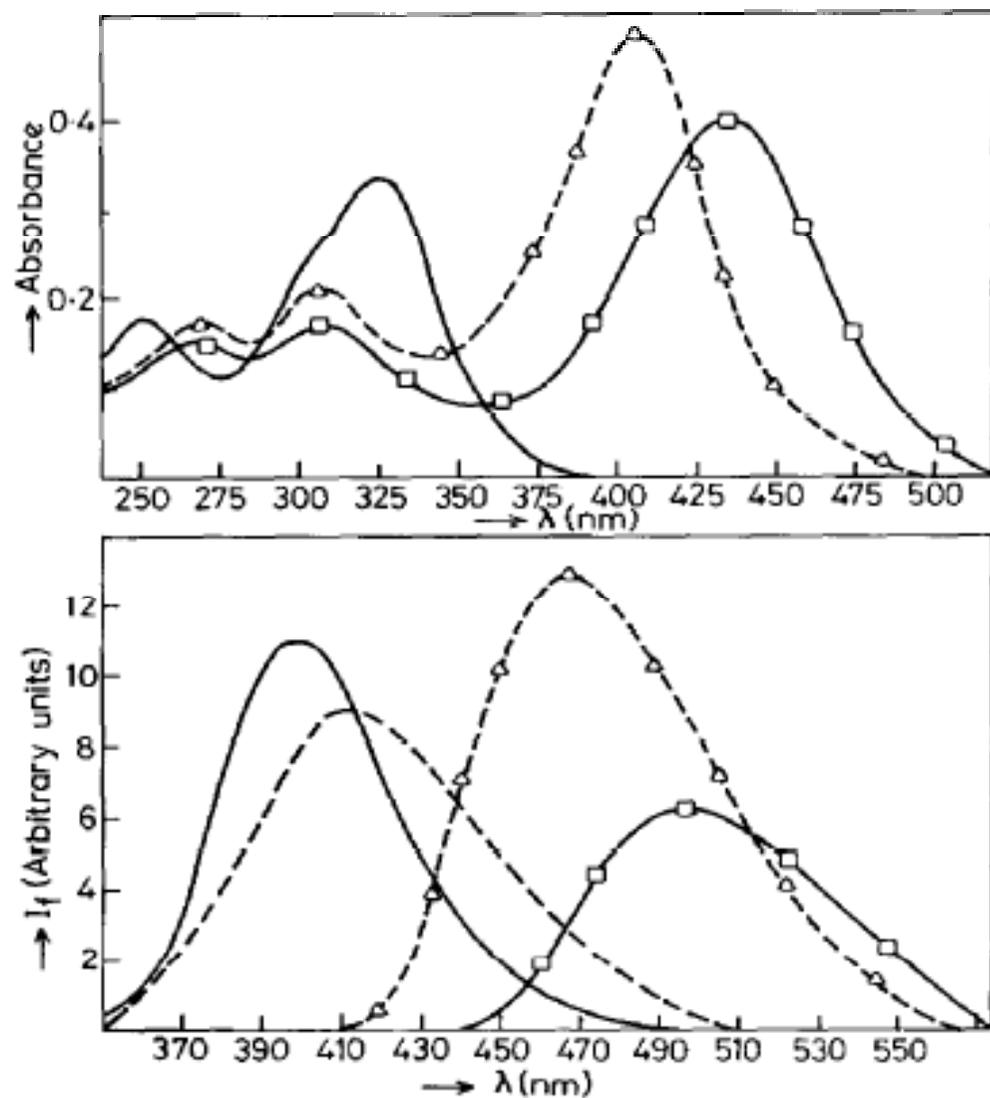


Fig. 3. Absorption (top panel) and fluorescence (bottom panel) spectra of different prototropic species of 2-benzoylfluorene: —, neutral; —□—, monocation; —△—, dication; — — —, monocation in cyclohexane medium.

Toth Mihaly, Chem. Phys. 46 (1980) 437-443).

THE TRIPLET-TRIPLET ABSORPTION OF CYCLOHEXADIENE-1,3 AND ERGOSTEROL.
SENSITIZED TOTAL GROUND STATE DEPLETION OF DIENES BY TRIPLET ENERGY TRANSFER
FROM THE RUBY LASER EXCITED 2-FLUORENYLPHENYLKETONE*

Received 5 February 1979;

Revised manuscript received 5 June 1979; in final form 17 August 1979

The triplet-triplet absorptions of cyclohexadiene-1,3 and ergosterol were determined in benzene at 22°C. The ground state depletion of these simple conjugated molecules via energy transfer from the triplet state of 2-fluorenylphenylketone under frequency doubled ruby laser excitation was shown to be a convenient method for studying the triplet states of dienes. From these total ground state depletions, triplet extinction coefficients were determined for 2-fluorenylphenylketone, cyclohexadiene-1,3, and ergosterol.

3.1. *Outline of the method [IS] – (18)M. Toth, forthcoming paper in this journal.*

2-Fluorenylphenylketone (FPK) has a strong and broad T-T absorption in the visible spectral region and a strong absorption band at 325 nm ($\epsilon = 2.76 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) which is highly bleachable (=89%). The unreactive 3T_1 state at 58 kcal mol⁻¹ is efficiently populated by a doubled ruby laser according to the following equation

$$nT(\text{FPK}) = w_{TT}(\text{FPK}) - n_{TT}(\text{FPK}) \cdot 10^{-\epsilon_T(347) \cdot I} \quad (1)$$

where nT is the concentration of triplet molecules, $\epsilon_T(347) = 7.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ is the S-S extinction coefficient at 347 nm, and I is the depletion intensity. I is related to the incident laser intensity, I_0 , to a good approximation as $\log(I_0/I) = \epsilon_T(347) \cdot nT \cdot X$, where $\phi_T = I$ is the triplet yield, $\epsilon_{TT}(347) = 2.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ is the T-T extinction coefficient at 347 nm, and $X = 0.6 \text{ cm}$ is the laser light path.

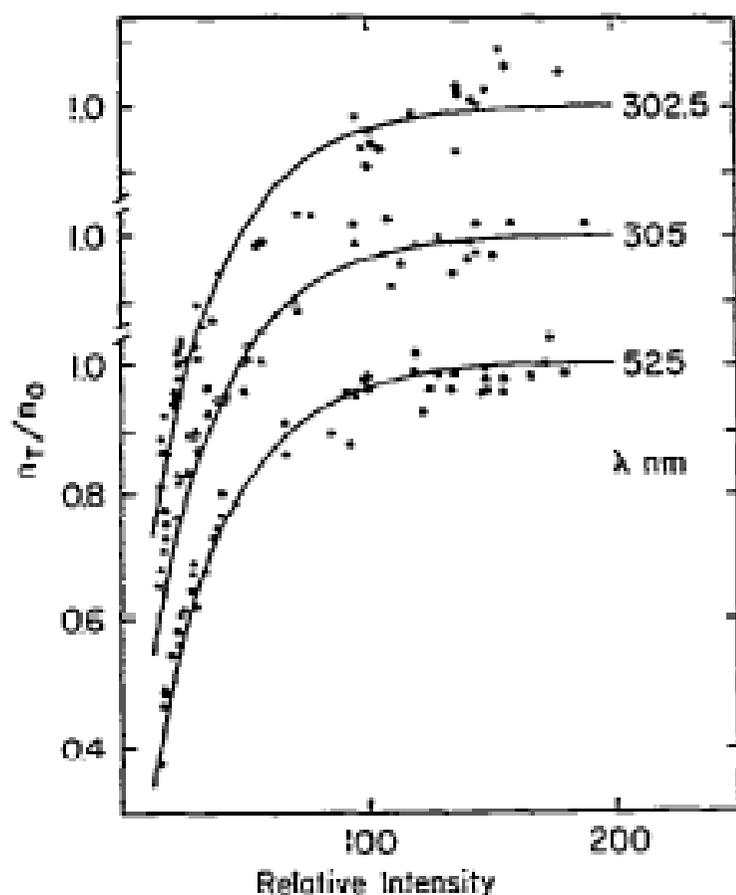


Fig. 2. Ground state depletion of 2-fluorenylphenylketone (525 nm), ergosterol (305 nm), and cyclohexadiene-1,3 (302.5 nm) observed as triplet formation at the wavelengths indicated. Slit width: 3.5 nm; solvent: benzene at 22°C. The line is traced following the results of FPK ground state depletion. The relative intensity of 100 corresponds to an absolute (incident) intensity of 1.3×10^{17} quanta cm^{-2} at 347 nm.

Table I
Total ground state depletion of 2-fluorenylphenylketone observed by triplet absorption at 525 nm (ΔD_{525})^{a)}

$I_U(\pm\%) \times 10^{-15}$ ^{b)} (quanta cm^{-2})	$\Delta D_{525}(\pm\%)$ $l = 1 \text{ cm}$	ΔLS ^{d)} ($\pm\%$)	$\epsilon_T(525) \times 10^{-4}$ ($\text{M}^{-1} \text{cm}^{-1}$)
1.1 (17.5)	0.536 (0.8)	0.6	1.88
1.2 ^{c)} (16.9)	0.526 (0.8)	1.6	1.84
average	(0.8)	(1.1)	1.86

a) 2.86×10^{-5} M in benzene.

b) Absolute laser intensity per relative intensity.

c) Experiment in the presence of 1.1×10^{-3} M of ergosterol.

d) Least-squares errors in ΔD_{525} .