Excited state interactions in phenol/olefin bichromophoric compounds: direct detection of an intramolecular exciplex

Francisco Galindo, M. Consuelo Jiménez, Miguel A. Miranda* and Rosa Tormos

Departamento de Química-Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Camino de Vera s/n, Apdo 22012, 46071 Valencia, Spain. E-mail: mmiranda@qim.upv.es

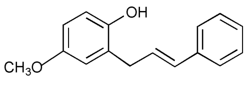
Received (in Liverpool, UK) 22nd June 2000, Accepted 2nd August 2000
First published as an Advance Article on the web 29th August 2000

The emission from an intramolecular exciplex detected in *trans*-4-methoxy-2-(3-phenyl-2-propenyl)phenol (1) is the first direct evidence for the excited state interchromophoric interaction in phenol–styrene systems.

Bichromophoric compounds have attracted considerable interest as models for the understanding of energy or electron transfer processes. They have also found application for mimicking some biological processes (*i.e.* photosynthesis) and for the development of new materials such as photoconducting polymers.[1]

trans-2-Cinnamylphenols are bichromophoric compounds containing phenol and styrene subunits connected by a methylene spacer. Upon the introduction of suitable substituents, these simple systems allow the reproduction at will of a wide range of intramolecular proton, electron or energy transfer processes.[2]

Previously, the photochemical reactivity of *trans*-2-cinnamylphenols and their relatively low fluorescence quantum yields, as compared with models containing the isolated chromophores, has been attributed to an intramolecular interaction in the excited state between the two chromophores.[3] However, no direct evidence has been provided in support of such interaction. In the present work, direct detection of an intramolecular exciplex has been achieved in the case of *trans*-4-methoxy-2-(3-phenyl-2-propenyl)phenol (**1**), by measuring the emission spectra in acetonitrile. To our knowledge, this is the first case of an intramolecular exciplex involving a phenol chromophore.



1

The emission properties of **1** are summarized in Table 1, together with those measured under the same conditions for the isolated 4-methoxyphenol chromophore. Thus, the fluorescence spectra of **1** in hexane displayed a single band with λ_{max} = 320 nm, clearly attributable to emission from the lowest lying phenolic singlet (compare trace B, Fig. 1a with trace A, Fig. 1b). The same result was obtained by exciting either at 250 nm (styrene) or at 290 nm (phenol), clearly due to efficient energy transfer between the excited singlets of both chromophores (Fig. 1c). By contrast, a completely different behaviour was observed in the more polar solvent acetonitrile. The most remarkable result was the presence of a much longer wavelength band centered at 420 nm and the concomitant disappearance of the phenolic emission at 320 nm (see Fig. 1b). This new band is clearly attributable to a charge-transfer

Table 1 Photophysical data of **1** and the reference compound 4-methoxyphenol in hexane and acetonitrile at room temperature[a]

Compound	Solvent	$\lambda_{emission}$/nm	ϕ_F	τ_F(ns)
1	Hexane	320	0.056	1.0
	Acetonitrile	420	0.051	5.1
4-Methoxyphenol	Hexane	320	0.143	1.9
	Acetonitrile	320	0.141	2.1

[a] $\lambda_{excitation}$ = 290 nm.

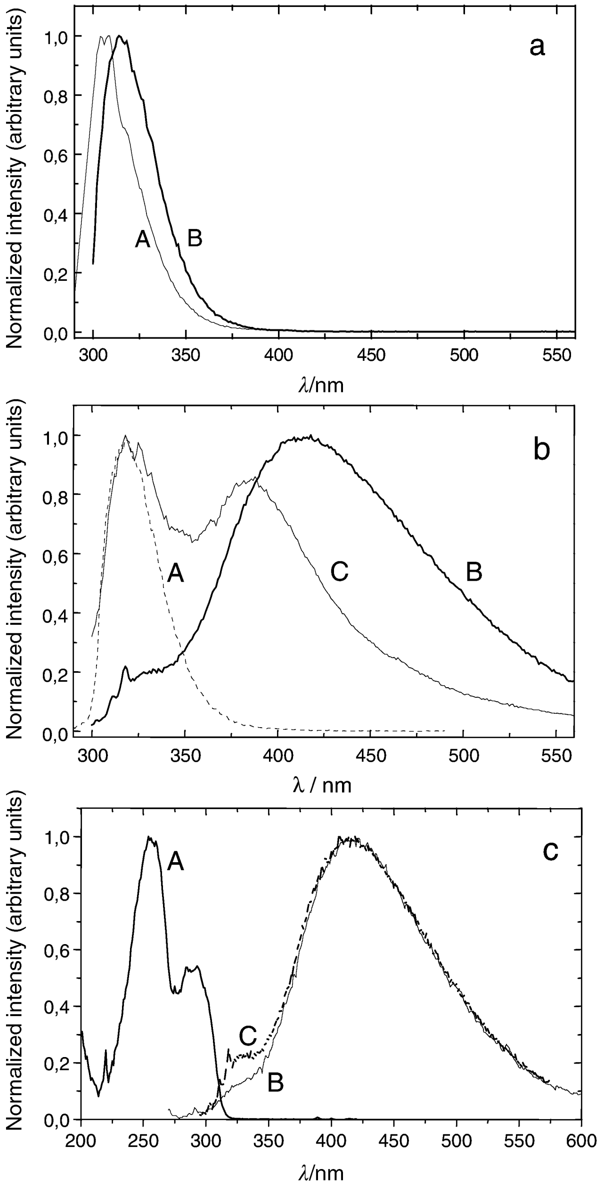


Fig. 1 Fluorescence spectra of: (a) the isolated β-methylstyrene (trace A) and 4-methoxyphenol (trace B); (b) **1** in hexane (trace A), in acetonitrile (trace B) and in a 9 : 1 dichloromethane–acetonitrile mixture (trace C); (c) **1** in acetonitrile; excitation spectrum (trace A), emission upon excitation at 250 nm (trace B) and emission upon excitation at 290 nm (trace C).

DOI: 10.1039/b005026l

exciplex, whose formation would be exergonic according to the Rehm–Weller eqn (1)[4]

$$\Delta G_f\,(\text{kcal mol}^{-1}) = 23.06\,(E_{D/D^{+\cdot}} - E_{A/A^{-\cdot}}) - E^* \quad (1)$$

where $E_{D/D^{+\cdot}}$ and $E_{A/A^{-\cdot}}$ are the redox potentials of the donor and acceptor moieties, and E^* is the singlet energy of the phenolic chromophore. Using the excitation energy determined from the intersection between normalized excitation and emission spectra, together with the reported literature values for the redox potentials,[5] the resulting Gibbs free energy associated with exciplex formation would be *ca.* −25 kcal mol^{-1}. The emission spectra were also obtained for solutions of **1** in solvents of intermediate polarity and in a variety of solvent mixtures. For instance, using CH_2Cl_2–CH_3CN (9 : 1, v : v), both the monomer and the exciplex bands were observed (see trace C, Fig. 1b). As expected for a charge-transfer exciplex, the position of the longer wavelength band showed a clear dependence on the solvent polarity (see Fig. 2 for the Lippert–Mataga plot with the data obtained in pure solvents).[6]

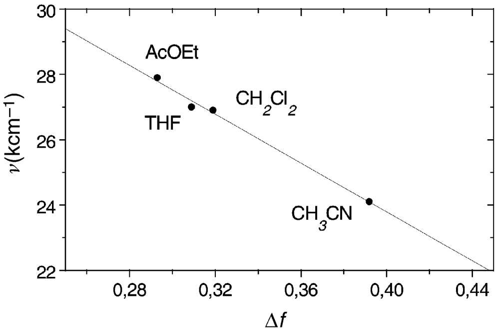


Fig. 2 Solvent polarity dependence of the exciplex emission maxima for **1**. Solvent parameter Δf has been calculated as follows: $\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(4n^2 + 2)$ where ε is the dielectric constant and n is the refraction index of the solvent.

The quantum yield of emission at 420 nm was 0.05, and the lifetime was relatively long (5.1 ns), as compared with the monomer under the same conditions (1.0 ns). The exciplex was quenched by oxygen (k_q = 4.2 × 10^{10} M^{-1} s^{-1}) and by tetrabutylammonium hydrogensulfate (k_q = 3.3 × 10^9 M^{-1} s^{-1}). The Stern–Volmer plot for quenching by the ammonium salt is shown in Fig. 3. Similar salt effects have been observed for other exciplexes; they have been attributed to dissociation into radical ions, with the concomitant decrease of fluorescence.[7]

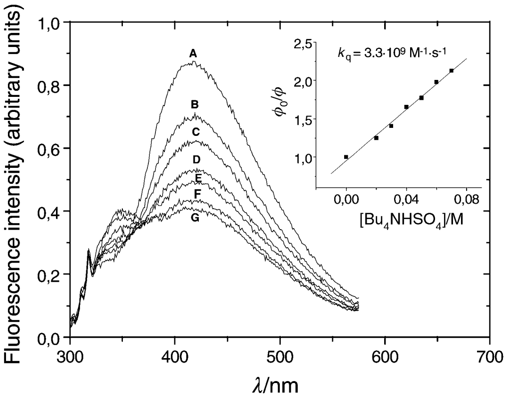
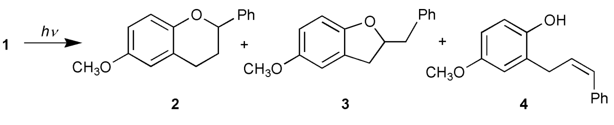


Fig. 3 Quenching of the exciplex fluorescence for **1** by [Bu_4NHSO_4] at different molar concentrations: curve A) 0.0 M; B) 0.02 M, C) 0.03 M, D) 0.04 M, E) 0.05 M, F) 0.06 M, G) 0.07 M.

All the above data were obtained using 5 × 10^{-5} M solutions of **1**. To check whether the corresponding intermolecular exciplex is also observable, equimolar mixtures of 4-methoxyphenol and β-methylstyrene in acetonitrile (5 × 10^{-5} M each) were studied. The emission spectra consisted of the bands assignable to the isolated chromophores (either phenolic maximum at 320 nm, upon excitation at 290 nm, or styrenic maximum at 310 nm when exciting at 250 nm). However, using much higher concentrations of the partners (0.1 M), the exciplex emission at *ca.* 440 nm was clearly observable.



	2	3	4
Benzene	86%	10%	4%
Acetonitrile	99%	traces	traces

Scheme 1

After determining the photophysical properties of **1**, its preparative photochemistry was also investigated. Irradiation of **1** for 1 h in acetonitrile and benzene, with the Pyrex-filtered light of a medium pressure Hg lamp resulted in the almost complete (> 95%) consumption of the starting material, accompanied by formation of the six-membered ring compound **2** as the major photoproduct. Minor amounts of the *cis*-isomer **4** and the five-membered ring product **3** were also obtained in benzene. These results are summarized in Scheme 1.

As the formation of six-membered ring product **2** is considered to be an indication for the involvement of intramolecular excited state electron transfer,[2] detection of a charge-transfer exciplex is compatible with the preparative photochemistry of **1**.

In summary, the intramolecular excited state interaction between phenol and styrene has been directly observed for the first time as an exciplex emission. This strongly supports the previous mechanistic proposals to explain the photochemistry of bichromophoric cinnamylphenols. Although such interaction is reported here for a single compound (**1**), preliminary data in hand show that other analogues with electron donating substituents at the phenolic ring [such as 4-methyl, 4,6-dimethyl- and 4,6-di-*tert*-butyl-2-(3-phenyl-2-propenyl)phenol] exhibit similar photophysical and photochemical properties.

Financial support by the DGICYT (PB 97-0339) is gratefully acknowledged. M. C. J. thanks the European Commision for a grant (MCFI-1999-00101). F. G. thanks Ministerio de Educación y Cultura for a grant.

Notes and references

1 S. Speiser, *Chem. Rev.*, 1996, **96**, 1953; V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood Limited, Chichester, 1991; D. Gravel, S. Gauthier, F. Brisse, S. Raymond, M. D'Amboise, P. Messier, B. Zelent and G. Durocher, *Can. J. Chem.*, 1990, **68**, 908; E. Cotsaris, J. W. Verhoeven and N. S. Hush, *J. Am. Chem. Soc.*, 1987, **109**, 3258.

2 M. C. Jiménez, F. Márquez, M. A. Miranda and R. Tormos, *J. Org. Chem.*, 1994, **59**, 197; M. C. Jiménez, P. Leal, M. A. Miranda and R. Tormos, *J. Org. Chem.*, 1995, **60**, 3243; M. C. Jiménez, M. A. Miranda and R. Tormos, *Tetrahedron*, 1997, **53**, 14 729; M. C. Jiménez, M. A. Miranda and R. Tormos, *J. Org. Chem.*, 1998, **63**, 1323; M. C. Jiménez, P. Leal, M. A. Miranda, J. C. Scaiano and R. Tormos, *Tetrahedron*, 1998, **54**, 4337.

3 M. T. Bosch-Montalvá, L. R. Domingo, M. C. Jiménez, M. A. Miranda and R. Tormos, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2175.

4 A. Weller, *Z. Phys. Chem.*, 1982, **133**, 93.

5 E_{ox} for 4-methoxyphenol is +0.406 V *vs.* SCE and E_{red} of β-methylstyrene is −2.54 V *vs* SCE as reported in *Technique of Electroorganic Synthesis*, ed. N. L. Weinberg, part 2, John Wiley & Sons, New York, 1975.

6 N. Mataga, *Adv. Chem. Phys.*, 1999, **107**, 431; *The Exciplex*, ed. M. Gordon and W. R. Ware, Academic Press, New York, 1975.

7 B.-W. Zhang, Y. Cao, J.-W. Bai and J.-R. Chen, *J. Photochem. Photobiol., A: Chem.*, 1997, **106**, 169.