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Fluorescence quenching in organogel as a reaction medium

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Abstract

The quenching of the anthracene fluorescence by amines has been used as a probe reaction for the determination of electron-transfer quenching rate in an organogel medium. From the Stern–Volmer analysis of the emission (steady-state and time-resolved) it has been found that quenching constants do not differ significantly in the liquid solution and in the organogel. Eventually, if the appropriate donor is used, the photoinduced electron-transfer reaction can be a diffusion-controlled process in the self-organised medium.

Keywords: Fluorescence quenching; Stern–Volmer; Photoinduced electron-transfer; Diffusion rates; Anthracene; Organogels; Gels; Self-assembly

1. Introduction

Research on organogels and hydrogels has been intensive during the last years due to their physical properties but also because of their applicability to practical problems, from biomedical to waste treatment studies. The study of such a special kind of materials has been approached mainly from the viewpoint of rheology but also much attention has been paid to the specific chemical interactions leading to the formation of supramolecular assemblies [1]. Gels are formed either by macromolecules or by small molecules that, in amounts typically of 1–2% in weight, or even less, impart a solid-like aspect to a solution. Despite of the large effort devoted to the physical understanding of gels, little attention has been paid to the very interesting possibility of carrying out chemical reactions in those organised media. Some authors have studied recently the reactions in the boundaries of the gel fibres with good results [2]. In order to explore the use of organogels as organised media for chemical reactions, it is essential to be able to analyse how much the formation of the gel network can affect to the reaction rates. Here we have explored the reactivity far away from the bundles of organogelator, by means of the kinetic study of a well-known photoinduced electron-transfer (eT) process.

In the course of our research on peptidomimetic molecules [3,4] it was found that small amounts of some macrocyclic derivatives where able to promote the gelation of different organic solvents. The small peptidomimetic molecule **1** (Chart 1), synthesized using two amino acids (L-valine) connected by one aromatic and one aliphatic spacer, was selected in this work to create the appropriate organogel reaction medium [3a,c].

On the other hand, the reduction of aromatic hydrocarbon excited states by amines was selected as the probe reaction, using anthracene as electron acceptor, (Scheme 1), since those are fast processes easy to monitor by means of the concomitant fluorescence quenching, and the reaction rates can be determined by means of a Stern–Volmer analysis [5].

Our goal was to investigate the kinetics of a well-known photochemical transformation in order to deduce indirectly the order of magnitude of the diffusion constant in organogel medium. To our knowledge this is the first time that a self assembled organogel has been used as medium for the determination of fluorescence quenching rates. The information derived from such study could seed some light to the understanding of gel chemistry. The reasons for the choice of an excited-state electron-transfer reaction are the following: (1) introduction of energy in the form of light, instead

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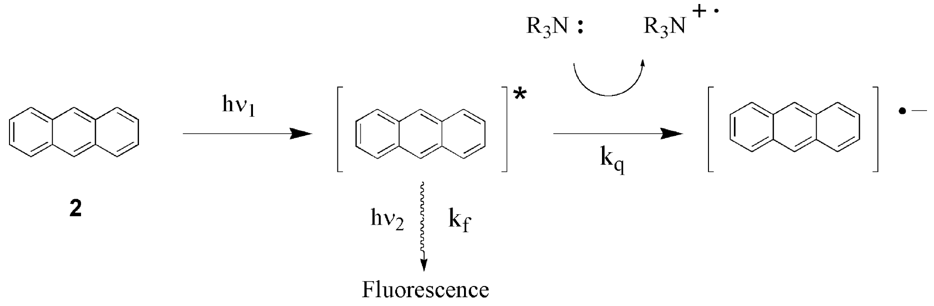
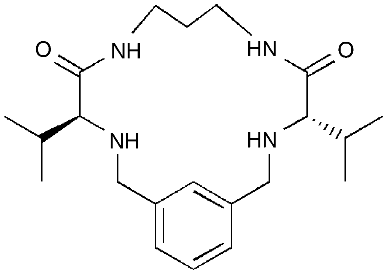


Scheme 1.



1

Plate 1.

of heat, allows to maintain intact the network of fibres in the organogel. (2) The high molar extinction coefficient of anthracene allows to load the gel with a very low concentration of probe, preventing the occurrence of ground state interactions with molecules of gelator. (3) The high emission of anthracene allows the use of non-invasive techniques like steady-state and time-resolved fluorescence spectroscopies to monitor the extent of the process and hence to calculate the bimolecular rate constants.

2. Experimental

All chemicals were obtained from Aldrich in the highest purity grade. Anthracene was recrystallized from ethanol twice. Spectroscopy grade solvents were used for this study. Synthesis of **1** [3b] and gel properties [3a,c] were described previously. Gel preparation was done by dissolving 12 mg of **1** in 3 ml of hot toluene, followed by introduction of the solution in a quartz fluorescence cell (1 cm × 1 cm), and allowing the hot liquid to cool to room temperature (typically gelation takes place a few degrees before reaching room temperature). Due to the high transparency of these organogels, no special setup was needed to carry out standard measurements.

The *emission/excitation spectra* were recorded in a Varian Cary Eclipse fluorimeter equipped with a xenon flash lamp. *Lifetime measurements* were recorded with the technique of time correlated single photon counting (TCSPC) in an IBH equipment using a pulsed nanosecond hydrogen lamp (0.5 bar, 1.0 ns pulse width). The fitting analysis was done using the software provided by IBH.

3. Results and discussion

An organogel was prepared as described above from macrocycle **1** (0.4%, w/w) and toluene, containing 2×10^{-5} M of anthracene. No ground-state interaction seems to take place between the probe anthracene and the networks created by the organogelator, since the emission/excitation spectra and the lifetime of the probe in gel medium match those in liquid toluene (Figs. 1 and 2).

Addition of triethylamine (TEA) to the gel (previously warmed to allow the addition of the quencher to a fluid solution, and afterwards cooled to r.t. to form the gel) did not interfere with the gel formation but lead to the partial quenching of the emission.

According of the Stern–Volmer scheme [6] the intensities of the unquenched (I_0) and partially quenched (I) emissions are given by Eqs. (1) and (2), where K_{sv} is the Stern–Volmer constant, k_q the bimolecular quenching constant, τ the excited state lifetime of the probe and $[Q]$ the quencher concentration.

$$I_0/I = \tau_0/\tau = 1 + K_{sv}[Q] \quad (1)$$

$$K_{sv} = k_q \tau_0 \quad (2)$$

The intensities of anthracene fluorescence in organogel in the presence of TEA where fitted according to Eq. (1) yielding a value of $K_{sv} = (12.4 \pm 1.4)\,\mathrm{M}^{-1}$. Using

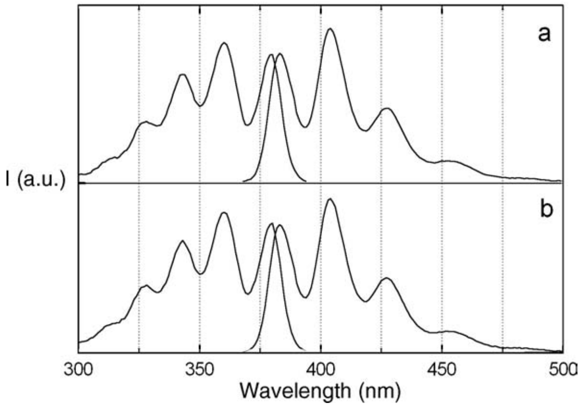


Fig. 1. Emission (right, $\lambda_{exc} = 358$ nm) and excitation (left, $\lambda_{em} = 404$ nm) spectra of anthracene (2×10^{-5} M) in (a) toluene gel and (b) liquid toluene solution.

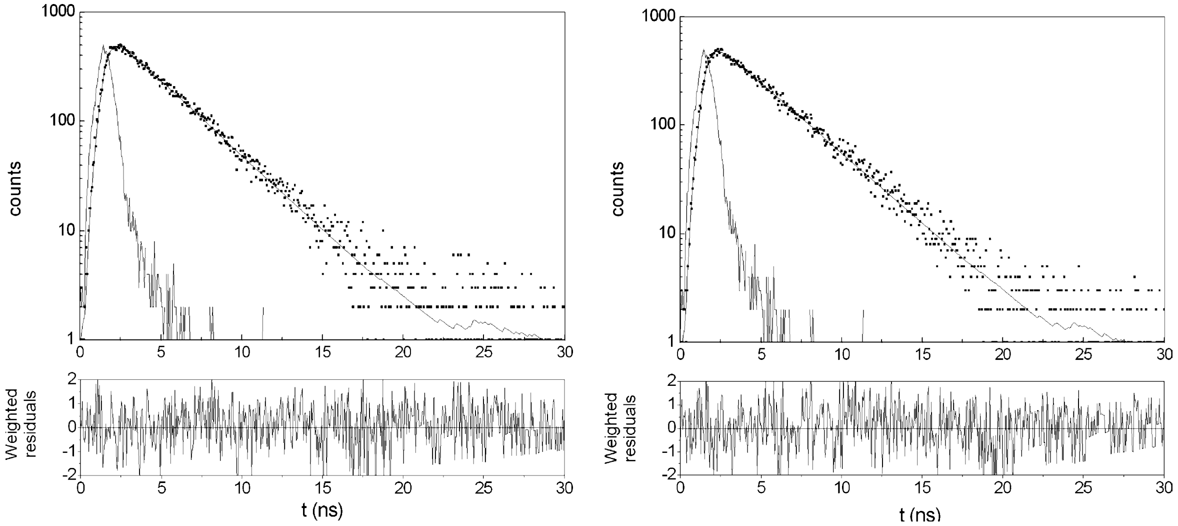


Fig. 2. Fluorescence decay curves of anthracene (2×10^{-5} M) in aerated toluene in liquid (left) and in gel state (right) [$\lambda_{exc} = 358$ nm/$\lambda_{em} = 404$ nm]. It is also shown the incident light pulse. Lifetimes: 3.1 ns (liquid), 3.3 ns (organogel).

the measured value for the fluorescence lifetime of anthracene in deoxygenated toluene ($\tau_0 = 3.8$ ns), the quenching constant for the bimolecular process was derived: $k_q = (3.3 \pm 0.4) \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$. The quenching constant of the same reaction in pure liquid toluene was also determined, yielding a $K_{sv} = (10.4 \pm 0.2)\,\text{M}^{-1}$ and a $k_q = (2.74 \pm 0.05) \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$. Both values are nearly coincident under the experimental error (Fig. 3).

In order to check that the fluorescence suppression is purely dynamic and not a combination of static and dynamic quenching, the experiments were repeated measuring the emission lifetimes with the technique of the time-resolved fluorescence spectroscopy. For the concentration range employed in these experiments the Stern–Volmer plots representing τ_0/τ were found to be linear and yielding K_{sv} values in the same order of magnitude as those calculated by the steady-state technique (see Table 1). Noteworthy, the quenching constant in organogel derived from the lifetime measurements was again slightly higher than that in liquid medium (Fig. 4).

The influence of viscosity in the fluorescence quenching is a well-established effect [7,8]. In order to confirm experimentally, in our conditions, that the decrease in quenching rate was applicable also to the probe reaction, a series of measurements in two liquids of similar polarity but different macroscopic viscosity were made. Thus, when methanol ($\eta = 0.551$ mPa s) [9] was employed as solvent a value of $K_{sv} = (4.22 \pm 0.05)\,\text{M}^{-1}$ was obtained. When the significantly more viscous fluid diethyleneglycol was used as solvent ($\eta = 29.99$ mPa s) [9], a smaller Stern–Volmer constant was found ($K_{sv} = (1.84 \pm 0.09)\,\text{M}^{-1}$). A recent study with anthracene and a different quencher in ionic liquids (with higher viscosity) determined an analogous drop in the K_{sv} for the more viscous medium [10].

The thermodynamics of the eT reactions are governed by their Gibbs free energy change, which can be estimated by

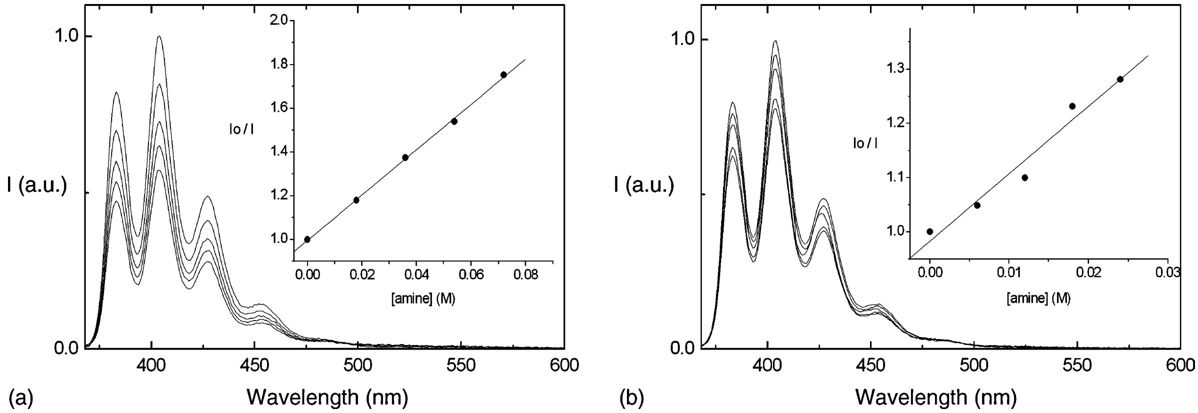


Fig. 3. Emission spectra ($\lambda_{exc} = 358$ nm) of anthracene (2×10^{-5} M) in the presence of increasing amounts of triethylamine: in liquid toluene (left) and in toluene organogel (right). Also included Stern–Volmer plots (insets).

Table 1
Collected data about the fluorescence quenching of anthracene with different quenchers in several media

Entry	Quencher	Solvent	State	K_{sv} (M^{-1})	k_q ($\times 10^9$ M^{-1} s^{-1})
1[a]	Triethylamine	Toluene	Liquid	10.4 ± 0.2	2.74 ± 0.05
2[a]	Triethylamine	Toluene	Gel	12.4 ± 1.4	3.3 ± 0.4
3[b]	Triethylamine	Toluene	Liquid	5.1 ± 0.5	1.3 ± 0.1
4[b]	Triethylamine	Toluene	Gel	9.7 ± 0.6	2.5 ± 0.2
5[a]	4-Butylaniline	Toluene	Liquid	71.5 ± 1.1	18.8 ± 0.3
6[a]	4-Butylaniline	Toluene	Gel	106 ± 12	28 ± 3
7[a]	Triethylamine	Methanol	Liquid	4.22 ± 0.05	[c]
8[a]	Triethylamine	Diethyleneglycol	Liquid	1.89 ± 0.09	[c]

[a] Steady-state measurement.
[b] Time-resolved measurement.
[c] Data not determined.

means of the Weller equation for non-polar solvents (Eq. (3)) [11].

$$\Delta G\,(\mathrm{kcal/mol}) = 23.06[E_d\,(\mathrm{V}) - E_a\,(\mathrm{V})] - E^*\,(\mathrm{kcal/mol}) \tag{3}$$

In Eq. (3), E_d and E_a are the redox potentials of donor and acceptor in their ground states and E^* is the energy of the excited state involved in the reaction (the first excited singlet of anthracene in this case). Introducing $E_d = +1.15$ V versus SCE for TEA [11] and $E_a = -1.95$ V versus SCE for anthracene [12] and E^* (S_1 of anthracene) = 76.1 kcal/mol [12], a $\Delta G = -4.6$ kcal/mol is derived. A more exergonic reaction, and in principle faster, could be obtained if replacing TEA by an easily oxidizable donor. Alkylanilines have lower oxidation potentials than TEA. Thus, the eT process between anthracene and a 4-alkylaniline would have an associated $\Delta G = -13.1$ kcal/mol, as calculated introducing $E_d = +0.78$ V versus SCE (corresponding to 4-methylaniline [12]).

Fluorescence quenching measurements where done with 4-butylaniline (4BA) as quencher and the Stern–Volmer analysis in gelated toluene yielded $K_{sv} = (106 \pm 12)\,M^{-1}$ and a $k_q = (2.8 \pm 0.3) \times 10^{10}\,M^{-1}\,s^{-1}$. The same measurements in liquid toluene afforded $K_{sv} = (71.5 \pm 1.1)\,M^{-1}$ and a $k_q = (1.88 \pm 0.03) \times 10^{10}\,M^{-1}\,s^{-1}$. The experiment with 4BA yields a limiting value for the reaction rate since the obtained k_q is approximately of the same order of magnitude as the diffusion constant in toluene ($k_{diff} = 1.2 \times 10^{10}\,M^{-1}\,s^{-1}$ according to the literature [12]).

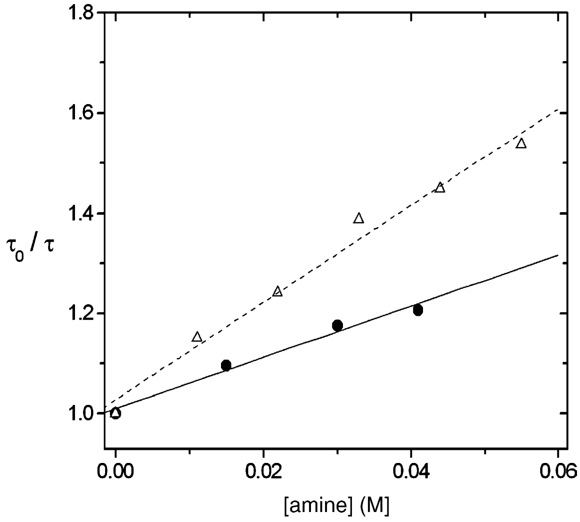


Fig. 4. Stern–Volmer fittings for the fluorescence quenching of anthracene (2×10^{-5} M) by triethylamine in liquid toluene (black circles) and in gelated toluene (white triangles).

For comparison purposes, the Stern–Volmer fittings of the steady-state quenching experiments can be seen in Fig. 5. In Fig. 6 the quencher effect on the fluorescence of the probe in organogel medium can be visualized. The calculated quenching constants are collected in Table 1.

A related approach was employed to study the dynamics of viscous solutions of a biopolymer in water [13]. Although the nature of the media (aqueous versus organic) and specially the kind of solute (biopolymer versus an small self-assembled organogelator) are different, the results here presented are pointing to the same underlying phenomenon. Although it has been demonstrated that diffusion-controlled photochem-

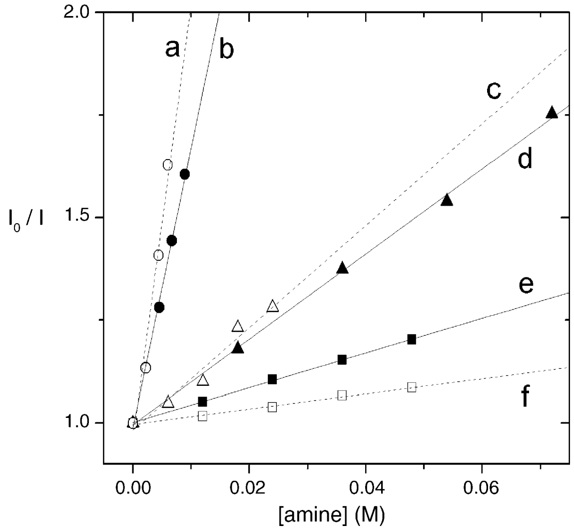


Fig. 5. Stern–Volmer fittings for the fluorescence quenching of anthracene (2×10^{-5} M) by amines in the following conditions: (a) gelated toluene and 4-butylaniline; (b) liquid toluene and 4-butylaniline; (c) gelated toluene and triethylamine; (d) liquid toluene and triethylamine; (e) liquid methanol and triethylamine; (f) liquid diethyleneglycol and triethylamine.

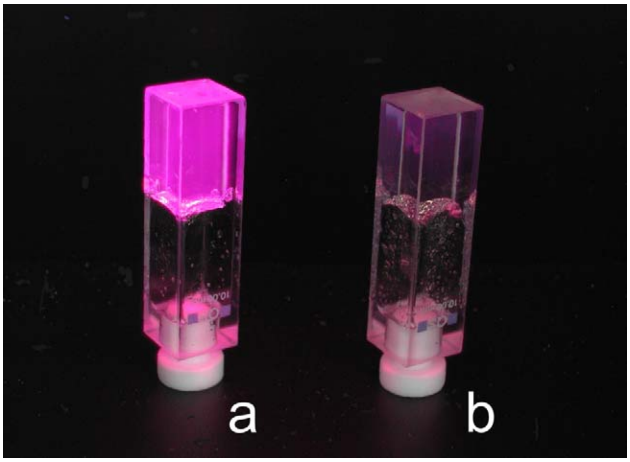


Fig. 6. Fluorescence quenching of anthracene (2×10^{-5} M) in gelated toluene: (a) without quencher and (b) in the presence of 3×10^{-2}M of 4-butylaniline. Picture has been taken under excitation at 365 nm.

ical reactions can be carried out in this kind of organogels, no conclusions can be drawn about the space where molecules can move freely, since the time window of these experiments is limited by the short lifetime of the excited probe. The results here reported are also in accordance with the conductivity measurements made recently in organogel media: it was reported that gelator molecules scarcely affected the ionic mobility of supporting electrolytes in a series of electrochemical experiments [14]. Also, studies with specific viscosity-sensitive probes pointed to the existence of *pools and channels of solvent* in organogels [15].

A last remark must be mentioned about the fact that in the experiments with organogels the fittings lie slightly above the parent experiments in liquids. To explain the differences, it could be pointed to a possible increase in local concentration of quencher due to the *volume exclusion effect* caused by the gelator network [16].

4. Conclusions

In summary, it has been shown that an standard photochemical electron-transfer reaction can take place in organogel medium *at a reaction rate analogous to that in pure liquid*, and with the appropriate donor/acceptor pair it is equivalent to the nanoscopic diffusion rate. Self-assembled organogels can represent a very interesting organised reaction medium for different organic processes as much as the gel state seems not to represent any limitation to the diffusion *at the nanoscopic level*, and hence many chemical reactions could take advantage of this particular feature.

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