

A Concept for Molecular Addressing by Means of Far-reaching Electromagnetic Interactions in the Visible

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Abstract

A pronounced concentration dependence of the time constant of fluorescence decay was found, disproving Strickler-Berg's equation restricting molecular light emission to a local process. Thus, interactions were found significantly extending to more than 100 nm and make such systems promising for interfaces between molecular dots or more complex molecular arrangements and conventional macroscopic electronics.

Keywords: Molecular electronics; Strickler-Berg-equation; Interfaces; Fluorescence

Introduction

The increasing demands of integration in electronic devices [1] makes the addressing of molecular structures attractive [2] where the operating frequency should be extended into the petahertz region [3]. Basic structures of molecular operating functional materials are promising candidates therefore where fluorescent chromophores exhibit the advantage of intermediate storage of the energy of excitation for further processing [4]. However, the addressing of local molecular structures starting by means of macroscopic electronics has still to be developed; the scanning tunnelling [5] and atomic force microscope are useful for such applications, however, hardly applicable for routine devices. Optical addressing is more attractive, however, limited by the optical resolution given by about half the wavelengths of about 250 nm in the visible known as Abbe's diffraction limit. Resolution beyond this limit is possible, however, hardly practicable for routine applications in electronics. An interface between the well-accessible conducting technology nodes of 25 nm to molecular structures of about 1 nm remains a challenge [6].

Materials and Methods

Dye 1 (CAS RN 110590-84-6) was prepared according to literature [7] Nile Blue A (CAS RN 3625-57-8) was purchased from Acros Organics, product code: 415690100. All solvents were used in spectroscopical grade, chloroform was purchased from Sigma Aldrich ($\geq 99.8\%$, contains 0.5–1.0% ethanol as stabilizer, product code: 1001744040), ethanol from Merck ($\geq 99.9\%$, water content $\leq 0.05\%$, index-No: 603-002-00-5). UV/V is spectra were obtained with a Varian Cary 5000 spectrometer. Fluorescence spectra were obtained with a Varian Cary Eclipse spectrometer, slit width 5 nm unless otherwise specified. Fluorescence lifetimes were measured with a NKT-Laser SuperK Extreme EXB-4 from NKT Photonics A/S as light source, an Edinburgh Instruments Ltd. monochromator and detected with a PicoHarp 300 from PicoQuant GmbH in combination with a PMA-C 192-N-M photomultiplier. Fluorescence lifetimes were obtained by exponential fitting of the deconvoluted fluorescence decays with a resolution of 8 ps. The fluorescence lifetime equals the negative reciprocal exponent. Excitation and detection wavelengths were steadily the corresponding relative spectral maxima, except the local maximum at 576 nm was applied in case of the detection of 1. All spectroscopic measurements were carried out in 1.000 cm quartz cuvettes.

Results and Discussion

Molecular addressing in the visible region (about 0.6 PHz) with operating chromophores with dimension of about 1 nm can be basically performed by means of electric dipole-dipole interactions where a theoretical concept was developed by Perrin [8] and further extended by Förster [9-12] (Förster resonance energy transfer, FRET) having established equation (1) for the quantitative description of the distance function R . For more recent discussion see [13].

$$k_{FRET} = \frac{1000 \cdot (\ln 10) \cdot \kappa^2 \cdot J_{DA} \cdot \Phi_D}{128 \cdot \pi^5 \cdot N_A \cdot \tau_D \cdot |R_{DA}|^6} \quad (1)$$

There are some mathematical constants in equation (1), the factor 1000 for the adaption to SI units and Avogadro's number N_A , some spectroscopic data of the involved chromophores where J_{DA} means the integral of the spectral overlap between the fluorescence spectrum of the energy donor and the absorption spectrum of the acceptor, Φ_D the fluorescence quantum yield and τ_D the fluorescence lifetime of the donor and the orientation factor κ . Important for molecular addressing is the dependence of the rate constant k_{FRET} on the inverse 6th power of the distance R causing a very fast damping. As a consequence, addressing by energy transfer extends over several nm where technology nodes of 25 nm or even larger and more distant seem to be hardly reachable. Influencing the emission of light from electronically excited molecules seems to be even more restricted where the basic theory for light emission was developed Perrin [14], Förster [15-16], Lewis and Kasha [17] and Strickler and Berg [18]. The latter established the generally accepted equation (2) known as the Strickler-Berg-Equation where τ_0 means the natural fluorescence lifetime and $A_{u \rightarrow l}$ Einstein's transition probability coefficient concerning to the lower (l) and upper (u) energetic level.

$$\frac{1}{\tau_0} = A_{u \rightarrow l} = 1000 \frac{8\pi \ln(10) c \tilde{\nu}_{u \rightarrow l}^2 n^2}{N_A} \frac{g_l}{g_u} \int \epsilon d\tilde{\nu} \quad (2)$$

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Received March 02, 2016; Accepted March 20, 2017; Published March 24, 2017

Citation: Langhals H (2017) A Concept for Molecular Addressing by Means of Far-reaching Electromagnetic Interactions in the Visible. J Electr Electron Syst 6: 215. doi:10.4172/2332-0796.1000215

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$$\frac{1}{\tau_0} = \frac{2.880 \cdot 10^{-9}}{\text{cm} \cdot \text{s}} n^2 \bar{\nu}_0^2 \frac{g_l}{g_u} \int \varepsilon d\tilde{\nu} \quad (3)$$

$$\tau = \phi \cdot \tau_0 \quad (4)$$

N_A means Avogadro's constant $\tilde{\nu}_{l \rightarrow u}$ the wavenumber of the electronic transition, c the velocity of light, n the index of refraction and g_l and g_u the degeneracies of the lower and the upper energetic state, respectively. There are some mathematical constants, the factor 1000 for the adaption to SI units and the integral extending over the absorption band, thus representing the oscillator strengths. The ratio of the degeneracies becomes unity for most complex organic chromophores because of low symmetry. The factors can be combined to the constant in equation (3) with $\tilde{\nu}_0$ being the mean wavenumber of the absorption band. The molar absorptivities of the maxima are proportional to the oscillator strengths for identical shapes of UV/Vis spectra. Equation (1) was established for strongly light-absorbing dyes ($\varepsilon \geq 8000$) with small geometrical distortion upon light absorption indicated by small Stokes' shifts [8]. The natural lifetime τ_0 can be interrelated with the apparent lifetime τ and the fluorescence quantum yield ϕ by means of equation (4).

Equation (2) essentially contains molecular properties of the fluorescent molecule and the index of refraction n of the molecular surrounding medium; a macroscopic influencing for data processing can be hardly expected on this basis.

The constancy of the fluorescence lifetime [19] implied by equation (2) was tested [20-22] by means of the fluorescent dye Nile blue chloride (CAS-RN 2381-85-3) in ethanol where a constant fluorescent lifetime of 1.42 ± 0.15 ns was reported for diluted solutions within 10^{-8} molar and 10^{-3} molar; for comparison: A fluorescence quantum yield [23] of 0.27 was reported for Nile blue perchlorate (CAS-RN 53340-16-2).

$$\tau = a \cdot \ln\left(\frac{c}{c^*} + 1\right) + b \quad (5)$$

We re-examined the concentration dependence of the fluorescence lifetime by means of the more stable Nile blue sulphate (CAS-RN 3625-57-8; the fluorescence lifetime slightly depends on the counter ion) and found the surprisingly strong dependence on the concentration of the dye shown in Figure 1. The concentration dependence of τ can be described by means of the previously developed equation (5) for solvent

effects where c^* is a characteristic concentration and a and b adjustable parameters; b means τ at infinite dilution and a the sensitivity.

There are various interactions of the chromophore of Nile blue with the molecular surrounding, where Coulomb interactions dominate because of the positive charge of the chromophore and the negatively charged counter ion. Thus, we applied the uncharged point symmetrical chromophore **1** (S-13; CAS- RN 110590-84-6, Figure 2) for extended investigation and the exclusion of any interference. The high fluorescence quantum yield [24,25] of **1** close to unity renders τ close to τ_0 and excludes influences by varying ϕ . The extraordinarily high light fastness [26] of **1** allows measurements even with long acquisition times. Starting with a highly diluted solution of $2.26 \cdot 10^{-5}$ molar of **1** in chloroform a time constant of the fluorescence decay of 5.04 ns was found where the dye molecules are well-separated by a mean intermolecular distance of 23 nm; for comparison the size of individual dye molecules extend to about 1 nm. A stepwise further dilution [27] until $1.08 \cdot 10^{-7}$ molar caused a decrease of the lifetime to 3.79 ns where the mean intermolecular distance became as high as 138 nm reaching macroscopic dimensions. Again, the concentration dependence of τ could be described by means of equation (5); see curve in Figure 3 and the linear correlation shown in the insert there. Interference by any molecular interactions was excluded by the application of Lambert-Beer's law (Figure 4, upper diagram) where a perfect linear correlation was obtained within the limits given by the precision of the spectrometer; a perfect linear correlation was also found for the concentration dependence of the fluorescence intensity; Figure 4, lower diagram. Moreover, the spectral band types both of absorption and fluorescence spectra were investigated and found to be congruently independent from the concentration. This can be interpreted as additional proofs for isolated, non interacting dye molecules in such highly diluted solutions.

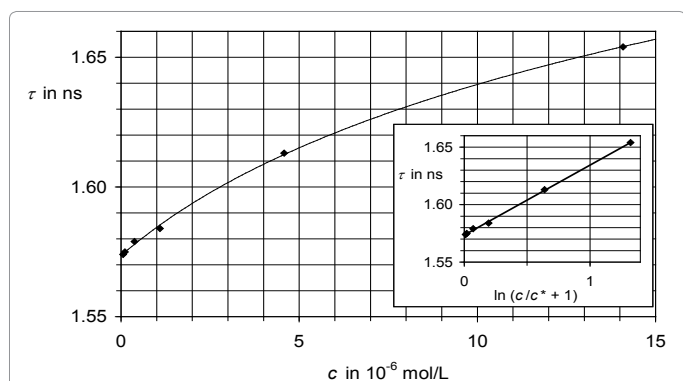
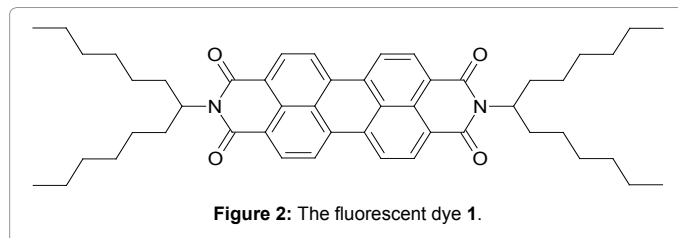


Figure 1: The time constant τ of fluorescence decay of Nile blue sulphate (CAS-RN 3625-57-8) in ethanol (25°C) as a function of the molar concentration c ; curve: Application of equation (5). Insert: Linear correlation for the application of equation (5); $c^* = 5.1 \cdot 10^{-6}$ mol·L⁻¹ slope 0.061 ns, intercept 1.574 ns, standard deviation 0.0009 ns, correlation number 0.9997 (6 points), $R^2 = 0.9993$.

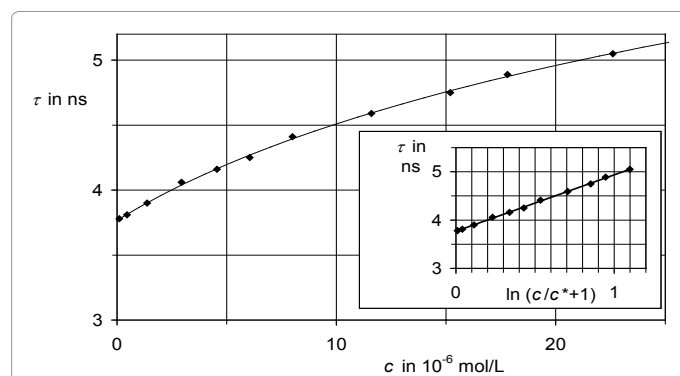


Figure 3: Dependence of the fluorescence lifetime τ of **1** in chloroform on the concentration c (diamonds; see Table 1). Curve: Function $a \cdot \ln(c/c^* + 1) + b$ according to equation (5) with $a=1.17$ ns, $c^*=1.17 \cdot 10^{-5}$ mol·L⁻¹ and $b=3.77$ ns. Insert: Linear correlation according to equation (5) (standard deviation 0.015, correlation number 0.9992, coefficient of determination 0.9984, 11 measurements).

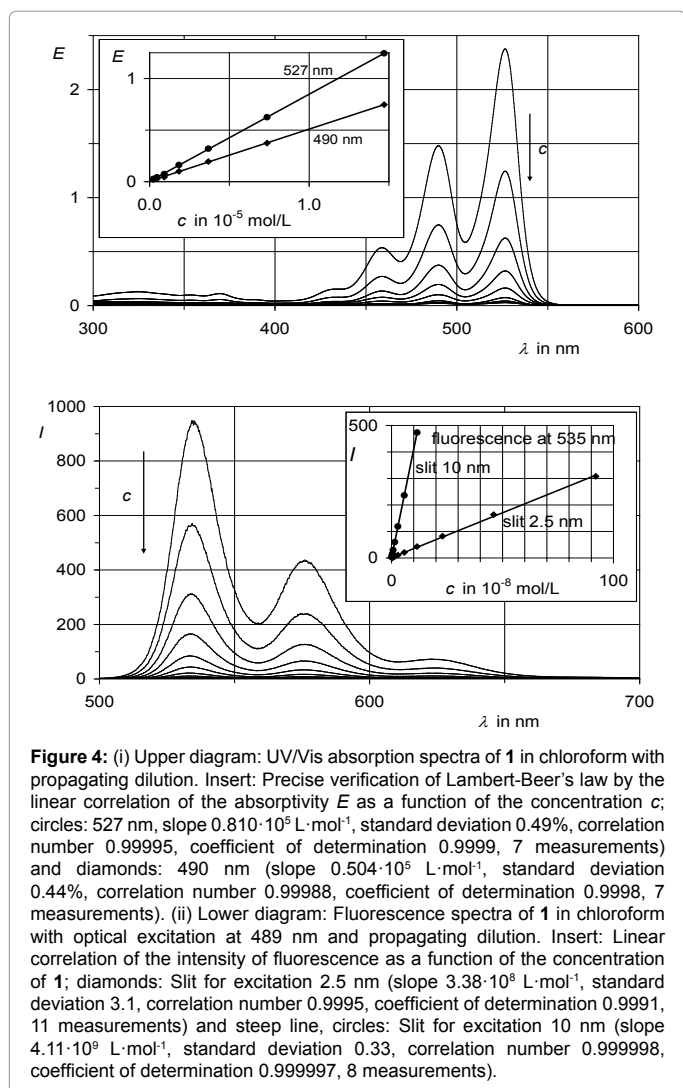


Figure 4: (i) Upper diagram: UV/Vis absorption spectra of **1** in chloroform with propagating dilution. Insert: Precise verification of Lambert-Beer's law by the linear correlation of the absorptivity E as a function of the concentration c ; circles: 527 nm, slope $0.810 \cdot 10^5 \text{ L} \cdot \text{mol}^{-1}$, standard deviation 0.49%, correlation number 0.99995, coefficient of determination 0.9999, 7 measurements) and diamonds: 490 nm (slope $0.504 \cdot 10^5 \text{ L} \cdot \text{mol}^{-1}$, standard deviation 0.44%, correlation number 0.99988, coefficient of determination 0.9998, 7 measurements). (ii) Lower diagram: Fluorescence spectra of **1** in chloroform with optical excitation at 489 nm and propagating dilution. Insert: Linear correlation of the intensity of fluorescence as a function of the concentration of **1**; diamonds: Slit for excitation 2.5 nm (slope $3.38 \cdot 10^8 \text{ L} \cdot \text{mol}^{-1}$, standard deviation 3.1, correlation number 0.9995, coefficient of determination 0.9991, 11 measurements) and steep line, circles: Slit for excitation 10 nm (slope $4.11 \cdot 10^9 \text{ L} \cdot \text{mol}^{-1}$, standard deviation 0.33, correlation number 0.999998, coefficient of determination 0.999997, 8 measurements).

The comparably strong concentration dependence of the fluorescence lifetime τ disproves the validity of equation (1) for real systems and is an indicator for long-reaching interactions up to macroscopic dimensions [28]. There are not only consequences for topics such as fluorescence lifetime spectroscopy (FLIM) including Förster resonance energy transfer processes (FRET), but offer completely novel possibilities such as for molecular electronics [6]. Thus, light emission resembles more the near field of a radio transmitter [29-30] than a molecular processes and is further treated with this concept. Firstly, the relative permittivity ϵ_r corresponding to the square of the refraction n of the medium has to be considered concerning the geometry. For the high frequency of light around 0.6 Petahertz the n_D at 589 nm is a good choice because this wavelengths is far away from absorption bands with interference by anomalous dispersion in the UV and the NIR of the commonly colorless solvents or polymeric optical media. Thus, resonating conducting structure become important with the dimensions of about $\lambda/(2n^2)$; this means about 125 nm in media such as chloroform ($n_D = 1.45$) or acrylic glass (PMMA, $n_D = 1.49$) and about 50 nm for structuring with $\lambda/(10n^2)$ for arrangements of passive resonators for the generation of travelling waves; compare, for example, the geometry of Yagi-Uda antennae [31-33] for TV frequencies. Such dimensions correspond to the strong

c	τ	l	d
$10^{-6} \text{ mol} \cdot \text{L}^{-1}$ [a]	ns ^[b]	nm ^[c]	nm ^[d]
22.6	5.04	42	23
17.8	4.91	45	25
15.2	4.77	48	26
11.6	4.59	52	29
8	4.41	59	33
6.05	4.29	65	36
4.56	4.13	71	40
2.94	4.05	83	46
1.37	3.9	106	59
0.456	3.82	154	85
0.108	3.79	249	138

Table 1: Fluorescence lifetimes τ of **1** in chloroform depending on the concentration c and the mean molecular distance d , respectively. Fluorescence excitation at 490 nm and detection at 535 nm.

[a] Molar concentration of dye **1** in chloroform. [b] Time constant τ for the exponential decay of fluorescence. [c] Calculated lengths of the cubic volume for one dye molecule [d] Calculated mean inter molecular distance [24] for **1**.

influence found on τ at intermolecular distance of 30 nm remaining still appreciable for more than 60 nm; Table 1.

On the other hand, the influencing of τ of a molecular step of light emission by means of structures extending to macroscopic dimensions offer novel possibilities in technology. There are many concepts for molecular electronics [6], however, the interface to the macroscopic electronics finally necessary for the data processing remains a challenge. The novel findings could help solving these problems by means of the connecting of the meanwhile in technical scale producible conducting technology nodes of 25 nm with operating molecular dots or more complex molecular arrangements.

Conclusion

The limiting Stickler-Berg equation (1) for molecular addressing implies isolated molecular processes of light emission, however, was disproved for real systems where long-reaching interactions until macroscopic dimensions were verified by means of the measurement of the concentration dependence of the fluorescence decay time constants τ and was quantitatively described with equation (5). The dimensions of such interactions resemble more near fields of radio transmitters than molecular processes and the reached significant distances between 30 and more than 60 nm make such systems promising for interfaces between molecular electronics and conventional macroscopic electronics.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie.

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