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Interpretation of fluorescence decay kinetics in 3-methylbenzimidazolyl(5′-5′)guanosine dinucleotides: exponential dependence on the number of phosphates in the polyphosphate bridge

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Abstract The number of phosphate groups in the 5′,5′-polyphosphate bridge of mRNA-cap dinucleotide analogues affects kinetics of long-range electron transfer (ET) responsible for 3-methylbenzimidazole (m^3B) fluorescence quenching in model dinucleotides. For instance, 3-methylbenzimidazolyl(5′-5′)guanosine dinucleotides (m^3Bp_nG, $n = 2, 3, 4$) having m^3B donor, 5′-5′ polyphosphate bridge, and guanine (G) acceptor, exhibit exponential dependence of the ET rate on the number of phosphates, i.e. donor–acceptor distance. Involvement of the 5′-5′ polyphosphate bridge in the ET is strongly indicated by lack of m^3B-G stacking effect on the exponential factor, which is the same at 20°C, where m^3B-G intramolecular stacking dominates, as that at 75°C where stacking–unstacking equilibrium is shifted in favour of the unstacked structure.

Keywords Nonexponential fluorescence decay · Q-exponential function · Base–base stacking interaction · Electron transfer

Abbreviations

ET	Electron transfer
G	Guanine
m^3B	3-Methylbenzimidazole
m^3BR	3-Methylbenzimidazole-1-β-D-ribofuranoside
m^3BTP	3-Methylbenzimidazole-1-β-D-ribofuranoside 5′-triphosphate
m^3Bp_nG	($n = 2, 3, 4$) di-, tri- and tetra-phosphate 3-methylbenzimidazolyl(5′-5′)guanosine
m^7G	7-Methylguanine

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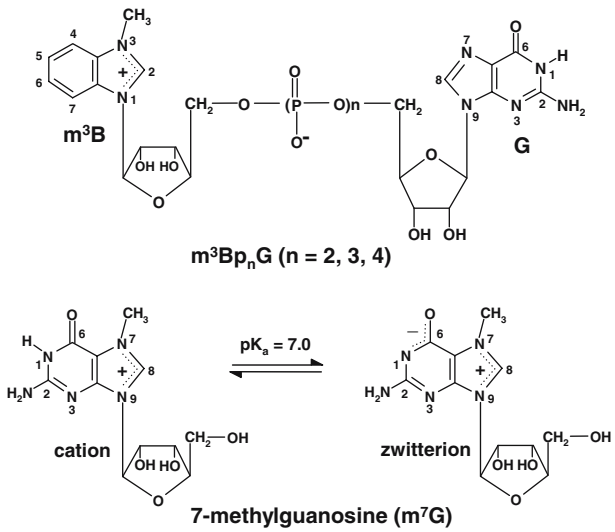
Introduction

Long-range electron transfers (ET) play key role in the numerous biological systems like proteins, cofactors, nucleic acids as well as energy transduction pathways of all living organisms. More than a half century of research (Libby 1952; Marcus 1956) has resulted in a remarkably detailed understanding of the distance- and driving-force factors affecting ET. It is now clear that electrons tunnel between sites in biological redox chains, and that molecular structures tune thermodynamic properties and electronic coupling interactions to facilitate these reactions. There are growing number of evidence indicating that the natural reactions are highly optimized, both in terms of thermodynamics and electronic coupling.

There are several reasons for extensive studies of long-range ET in nucleic acid systems, ranging from their biological function to possible applications in nanoelectronics. For example, photophysics of DNA ET provide a possibility to affect oxidative DNA damage from a distance in reactions that are sensitive to DNA mismatches and lesions. It was shown that DNA-mediated charge transfer between DNA-bound Ru(III) and protein leads to photoinduced oxidation of DNA-bound base excision repair enzymes (Yavin

et al. 2005, 2006). On the other hand, understanding of the mechanism of long-range ET (Bixon and Jortner 2002) is prerequisite for molecular materials designed to serve as active components in nanoscale devices. One of them could be DNA molecule due to its ability to transmit current (Giese 2000), but complexity of the system is still high challenge. It forms double helix, which consists of two complementary (hydrogen-bonded) chains of the π-stacked bases, each of them covalently bonded to one of the C(1′) atom of the two deoxyribose-phosphate chains located on both sides of the stacked bases. Some oligonucleotide cofactors contain more than one phosphate group in the phosphate-ribose bridge, e.g. two phosphates in the nicotinamide adenine dinucleotide (NAD) and flavin adenine dinucleotide (FAD), and three phosphates in the mRNA-cap end. In particular, the distance dependence of the ET rate has been shown to be complex function of individual parameters, including geometry and energetics (Nitzan 2001; Davies et al. 1998), albeit relative orientation of the donor and acceptor is often fixed (Bixon and Jortner 1999) due to limited rotational freedom. There are not to many rigid oligonucleotide systems, where donor, bridge and electron acceptor compounds allow investigation of the distance dependence of ET by keeping the donor–acceptor distance well defined, and the bridge electronic states unaltered. Usually the change of the length of the bridge affects the energy of the bridge electronic states, and thus modifies height of the barrier, and indirectly the donor–acceptor ET rate. Although these effects are hardly separated each other, they are prerequisite for understanding of ET. Nonetheless, because of the overlap between π-orbitals, it has been widely, and implicitly, assumed that long-range ET in DNA occurs universally via π-stacked chains of the base moieties, notwithstanding the existence of two phospho-ribose bridges and the aforementioned exceptions, where two or three phosphates are present in the polyphosphate bridges, which all may affect ET.

As was shown previously (Wieczorek et al. 1997; Kierdaszuk and Wlodarczyk 2006), 3-methylbenzimidazole ribofuranoside (Scheme 1, top), close structural analogue of the cationic form of N(7)-methylguanosine (Scheme 1, bottom), exists in the chemically fixed cationic form and is strongly fluorescent (λ_{max} 370 nm, $\Phi \sim 30\%$). We have used it to replace weakly fluorescent 7-methylguanine (m^7G) ($\Phi \sim 0.4\%$) in dinucleotide analogues of the mRNA-cap, which was validated by the fact that the positively charged m^7G moiety is bound by the eukaryotic initiation factor eIF4E (Marcotrigiano et al. 1997; Tomoo et al. 2002; Hu et al. 2003). Fluorescence intensity of 3-methylbenzimidazole-1-β-D-ribofuranoside (m^3BR) in dinucleotides is tenfold quenched relative to that of the free m^3BR in aqueous media due to static (Wieczorek et al. 1997) and dynamic (Kierdaszuk and Wlodarczyk 2006) quenching by intramolecular interactions in dinucleotides, including base–base stacking. It was applied previously in time-resolved studies on stacking interaction between the 3-methylbenzimidazole (m^3B) and guanine (G) moieties in model dinucleotides (Kierdaszuk and Wlodarczyk 2006). This was based on effect of base–base stacking on the continuous lifetime distribution, and mean value of fluorescence lifetime and parameter of heterogeneity derived from it. In contrast to picosecond decays of m^7G fluorescence (Wieczorek et al. 1997), m^3B fluorescence intensity decays of both m^3B-G dinucleotides and 3-methylbenzimidazole-1-β-D-ribofuranoside 5′-triphosphate (m^3BTP) were observed in the nanosecond range (Kierdaszuk and Wlodarczyk 2006), thus enable characterization of long-range ET in the nanosecond regime. Now we have extended previous studies to the mechanism of m^3B fluorescence quenching in model dinucleotides. We report here on the effect of the number of phosphates in the polyphosphate bridge of mRNA-cap dinucleotide analogues on the kinetics of long-range ET responsible for quenching of m^3B fluorescence in 3-methylbenzimidazolyl(5′-5′)guanosine dinucleotides (m^3Bp_nG, n = 2, 3, 4; Scheme 1).



Scheme 1 N(3)-methylbenzimidazolyl(5′-5′)guanosine dinucleotides (m^3Bp_nG, n = 2, 3, 4) containing cationic form of m^3B and neutral form of guanosine (pK_a 9.3) connected by di-, tri- and tetra polyphosphate bridges; and equilibrium between cationic and zwitterionic forms (pK_a 7.0) of the structurally similar N(7)-methylguanosine (m^7G). Note the different numbering systems for the two rings, according IUPAC

Materials and methods

Materials

3-Methylbenzimidazolyl(5′-5′)guanosine polyphosphates (m^3Bp_nG, $n = 2, 3, 4$; Scheme 1), and 5′-triphosphate of 3-methylbenzimidazole (m^3B) ribofuranoside (m^3BTP) were synthesized as described (Chlebicka et al. 1995). Tris–HCl buffer (pH 7.5) was made using Tris-(hydroxymethyl)-aminomethane hydrochloride (Merck, Darmstadt, Germany), HCl (Aldrich, Milwaukee, WI, USA) and MilliQ water (Millipore, Vienna, Austria).

Methods

Fluorescence intensity decays of 5 μM m^3Bp_nG ($n = 2$, 3, 4) in 20 mM Tris–HCl buffer (pH 7.50) at 20, 40, 60 and 75°C were measured using a picosecond time-correlated single-photon counting fluorometer as described previously (Kierdaszuk and Wlodarczyk 2006). The pH-values were adjusted for each temperature taking into account that for Tris buffers pH decreases 0.03 U per°C increase in temperature. Measurements of pH (±0.05) were with a CP315m (Elmetron, Zabrze, Poland) pH-meter equipped with a combination semi-micro electrode (Orion, Aylesbury, UK) and temperature sensor.

Fluorescence intensity decays data were analysed with power-like function (Eq. 1)

$$I(t) = A\left[1 - (1-q)\frac{t}{\tau_0}\right]^{1/1-q}, \quad (1)$$

where A is the amplitude (for normalized decay data $A = \tau_0/(2-q)$), τ_0 the mean value of lifetime distribution, and q is the parameter of heterogeneity describing the relative variance (ω) of fluctuations of fluorescence decay rates $\gamma = 1/\tau$ around the $1/\tau_0$ value

$$q = 1 + \frac{\left\langle (\gamma - \langle\gamma\rangle)^2 \right\rangle}{\langle\gamma\rangle^2} = 1 + \omega. \quad (2)$$

Hence, the heterogeneity parameter q provides information on distribution of fluorescence decay rates.

The power-like function was iteratively convoluted with the instrument response function, and results were compared with measured fluorescence decays using homemade procedures under Matlab (Kierdaszuk and Wlodarczyk 2006). The quality of fits was evaluated by the reduced chi-square values, and the structure observed in the plots of residuals normalized to error, i.e. residuals $= (I_{exp} - I_{theo})/\sqrt{I_{exp} + I_{theo}}$, where I_{exp} is the number of experimental counts, and I_{theo} is the number of counts resulted from convolution of the fitted function with instrument response function. Thus the I_{theo} is also subjected to experimental error, therefore was taken into account in normalization of residuals.

Long range electron transfer in dinucleotides

Electron transfer processes in model oligonucleotide systems usually occur between two bases surrounded by an electrically insulating environment medium, which represent barrier for the electrons. The electron must therefore tunnel from the electron donor to the electron acceptor through this insulating barrier. The phospho-ribose bridge between bases, and base–base interactions may affect ET. Surrounding molecular orbitals may act as virtual intermediates in this tunnelling process. Since the medium is not homogenous and has well defined structure, each element in this structure will be characterized by different electron tunnelling parameters. For description of many ET processes the medium is treated as homogeneous medium with uniform height of the barrier, which is sufficient to describe ET process.

In this simple case, the probability of the quantum mechanical tunnelling process fall of exponentially with the distance that separates the donor and acceptor molecules (Moser et al. 1992) due to the exponential dependence of the radial part of the wave function of the initial and final state. Application of Fermi's Golden rule to the ET reaction reveals that the reaction rate (Eq. 3) is determined by the product of the probability of the nuclear transition to occur, i.e. nuclear factor (the Franck–Condon term, FC), and the probability of the electron tunnelling to occur (electronic factor, V^2)

$$k_{ET} = (2\pi/h)V^2\mathrm{FC}, \quad (3)$$

where h is the Planck constant.

Taking into account that $V^2 = V^2_0 \exp(-\beta R)$, the distance dependence of the ET rate constant is

$$k_{ET} \propto \exp(-\beta R), \quad (4)$$

where R is the average edge to edge distance between the donor and acceptor molecules, β is an exponential coefficient that is characteristic for a certain medium. In many treatments of ET as a tunnelling process, the exponential factor β (called Gammov factor) was related to the height of barrier (W) by $\beta = (2mW)^{1/2}/h$, where m is the mass of the electron.

Results and discussion

Fluorescence decay rates

Decays of m^3B fluorescence intensity in m^3Bp_nG (n = 2, 3, 4) dinucleotides (Scheme 1) and m^3BTP in aqueous medium were analysed using lifetime distribution model and power-like decay function (Eq. 1) derived from it. In contrast to a widely accepted concept of discrete components in fluorescence decays exemplified by multi-exponential functions, our model is based on the idea of distribution of excited state lifetimes (Alcala et al. 1987; Lakowicz et al. 1987). We have shown (Wlodarczyk and Kierdaszuk 2003) that $1/\tau$ distribution is given by gamma function, which fulfil constraints of typical experiment and enable statistical treatment of fluorescence intensity decays leading to a simple analytical form of decay function (Eq. 1). The latter is described by two parameters, i.e. the mean value of lifetime distribution (τ_0)—characterizing kinetic of excited-state decay, and heterogeneity parameter (q)—objectively reflecting physical heterogeneity of the system (Eq. 2). It was shown previously (Kierdaszuk and Wlodarczyk 2006) that this model well describes m^3B fluorescence intensity decays in dinucleotides, while multi-exponential models were insufficient, and required a different number of exponential components, much more dependent on the quality of fits than on the physical model of the system. Therefore, we assumed that the mean values of lifetime distributions well define fluorescence decay rates ($k_0 = 1/\tau_0$), and their dependence on the number of phosphates in polyphosphate bridge is described below.

Exponential dependence of fluorescence decay rate on the number of phosphates

Fluorescence intensity decays of m^3B fluorophore in the m^3Bp_nG (n = 2, 3, 4) dinucleotides are subjected to two types of quenching phenomena. Some of them, like collisional quenching and ET between the m^3B and G base moieties of the intramolecular pair in dinucleotides are specific for dinucleotide structure, while others for nucleotide fluorophore. The latter include dynamic conformational equilibrium in the m^3B nucleotide, e.g. well known conformation of sugar moiety, and orientation of the m^3B base moiety around the C(1′)-N(9) glicosidic bond (Stolarski et al. 1996a; Ruszczynska et al. 2003), as well as collisional quenching by solvent. They are also present in m^3BTP, and are reflected by its fluorescence decay, which is not single-exponential. It seems that this is not caused by intermolecular stacking interactions, which are absent at low (5 μM) concentration of purine nucleotides in aqueous medium (Petersen et al. 1982). Excited-state proton transfer is also not possible due to a lack of the exchangeable N–H or O–H protons in the m^3B base moiety (Scheme 1). Intramolecular ET is not responsible for that either, because there is lack of a suitable electron acceptor within the m^3BTP molecule. It looks that solvent-mediated ET could be the most probable mechanism of m^3BTP fluorescence quenching, consistent with the fact that its fluorescence decay rate slightly depends on temperature.

Fluorescence intensity decay rate ($k_0 = 1/\tau_0$) of m^3B in the m^3B-G dinucleotides is equal to a sum of kinetic constants of all processes leading to a deactivation of its electronic excited state, i.e. $k_0 = k_r + k_q + k_{ET}$, where k_r is the radiative decay rate characterizing the excited state decay due to natural fluorescence in the absence of nonradiative processes; k_q is the rate of all nonradiative decays (k_i) caused by quenching processes other than ET ($k_q = \sum k_i$); and k_{ET} is the rate of nonradiative decay due to ^{i}ET. The m^3BTP fluorescence intensity decay rate (k_m), representing at each temperature a sum of k_r and k_q, was used here as a reference rate constant to compensate all quenching processes specific for nucleotide. We expect that resulted fluorescence decay rate ($k_0 = k_m + k_{ET}$) should reflect the m^3B-G interactions in m^3B-G dinucleotides, including stacking and ET between the m^3B and G base moieties.

Fluorescence decay rate values were determined for m^3Bp_nG (n = 2, 3, 4) dinucleotides at the temperature range 20–75°C (Fig. 1), where they exist in an equilibrium mixture of the unstacked and stacked intramolecular m^3B-G complexes, as independently confirmed by means of ^{1}H NMR at various pH and temperatures (Wieczorek et al. 1997). Intramolecular base–base stacking interaction was unequivocally shown for a numerous mRNA-cap dinucleotide analogues with the aid of ^{1}H NMR spectroscopy (Wieczorek et al. 1997; Stolarski et al. 1996a; Ruszczynska et al. 2003), fluorescence spectroscopy (Nishimura et al. 1980; Niedzwiecka et al. 2004) as well as molecular dynamic (MD) simulations (Stolarski et al. 1996b). All measurements were carried out at a concentration of 5 μM aqueous solutions of m^3Bp_nG dinucleotides, where intermolecular stacking association of purine nucleotides may be neglected (Petersen et al. 1982).

Since equilibrium between unstacked and stacked intramolecular m^3B-G complexes is strongly shifted in favour of the unstacked structures at temperatures above 60°C, where base–base stacking interactions are negligible low (Wieczorek et al. 1997; Jean and Hall

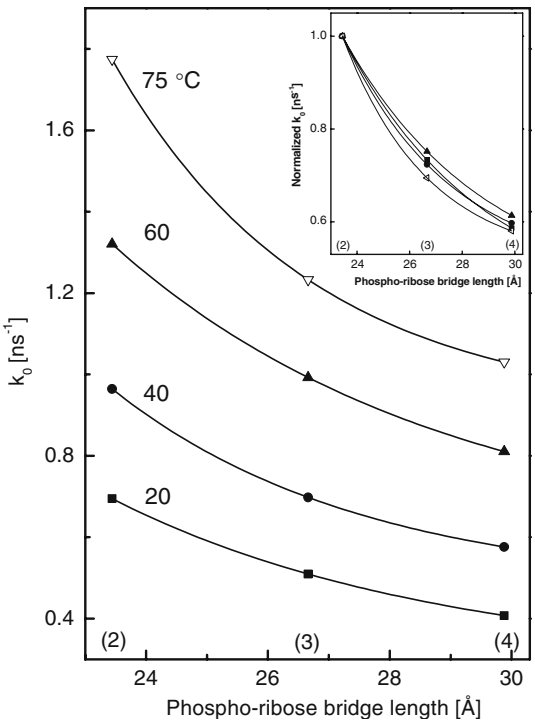


Fig. 1 Exponential dependence (*solid lines*) of m^3B fluorescence intensity decay rates ($k_0 = 1/\tau_0$) on the length of phospho-ribose bridges in m^3Bp_nG ($n = 2, 3, 4$) containing two, three and four phosphates (*numbers in brackets*), at temperatures indicated. *Inset* shows the same data normalized to unity for decay rate values of m^3Bp_2G at each temperature. The length of phospho-ribose bridges is equal to a sum of crystallographic lengths of all bonds (Mazza et al. 2000a, b) between the middle of C(4)–C(5) bond in each base moiety

2004; Kierdaszuk and Wlodarczyk 2006), temperature effect was used to evaluate mechanism of ET between m^3B and G base moieties in m^3B-G dinucleotides. Two routes of ET were considered, i.e. via molecular orbitals along phospho-ribose bridge or directly through space between overlapping molecular orbitals of one base with that of another in the base–base sandwich. The rate constant for ET is expected to be temperature-dependent for solvent-mediated transfer (Segal et al. 2000) or requiring base–base stacking interaction, but, not so for transfer through bonds of the bridge. Its dependence on the bridge length should be exponential (Eq. 4).

In accord with the foregoing, fluorescence decay rate (k_0) in dinucleotides decrease exponentially (Fig. 1) in function of polyphosphate bridge length (number of phosphates). Increase of temperature from 20 to 75°C shifts this exponential dependence to higher range of the k_0-values (Fig. 1). This may be caused by an intramolecular collisional quenching of m^3B fluorescence by G (see below), which increase with increasing temperature. Note, in particular, approximately the same exponential dependence of the k_0-values on the bridge length at each temperature (Fig. 1, inset), reflecting existence of the same mechanism of fluorescence quenching independently of temperature, being added confidence to the hypothesis that the phospho-ribose bridge participate in ET.

It is worth noticing that the electron donor (m^3B) and acceptor (G) of the intramolecular pair in dinucleosides have some probability of collision in the nanosecond time scale, which may lead to m^3B fluorescence quenching. If these collisions result in ET between the m^3B and G base moieties, its rate constant should increase with increase of temperature, which leads to higher probability of collision. However, Fig. 1 (inset) shows that these collisions do not affect the observed overall shape of exponential dependence of the k_0-values on the polyphosphate bridge length at temperature range 20–75°C. Thus ET, which may result from these collisions, does not depend on the length of polyphosphate bridge either. These and other temperature-dependent quenching phenomena, including intramolecular base–base stacking interaction, may be accounted for a temperature-dependent graduate shift of the exponential dependence in Fig. 1 towards higher values of the fluorescence decay rates.

We have tested that observed here dependence of the m^3B fluorescence decay rate ($k_0 = 1/\tau_0$) on the distance between electron donor (m^3B) and acceptor (G) in dinucleotides, i.e. on the ET efficiency can not be confirmed for free m^3B fluorophore in aqueous solution subjected to intermolecular quenching by G. This is due to high value of the minimal average distance between m^3B and G attainable in solution, which is at least two orders of magnitude higher than that in the m^3B-G dinucleotides (Fig. 1). One may readily calculate that at least millimolar concentrations of both m^3B and G are required to obtain an average distance between them similar to that in dinucleotides (Fig. 1), while their solubility is limited to several tens of μM. Consequently, at highest possible concentration of G (23 μM) in aqueous solution of m^3B, its fluorescence intensity decay was not affected by G quenching (data not shown). This points once again to a crucial role of the phospho-ribose bridge between the N(1) of m^3B and N(9) of G (Scheme 1) for electron tunnelling between them.

It clearly would have been desirable to determine the exponential factor β (Eq. 4) for all temperatures in spite of the limited number of m^3Bp_nG ($n = 2, 3, 4$) dinucleotides analogues available. Distance-dependent rate constant (Fig. 1) was fitted by equation $k_0 = k_m + k_{ET} = k_m + c\exp(-\beta R)$, where c is the rate constant at the van der Waals separation distance (Croney et al.

2003), and k_m is the m^3BTP fluorescence decay rate used here as a reference rate constant (see first paragraph of this Section) representing, at each temperature, a sum of all decay rates (k_r, k_q) excluding k_{ET}. In line with Fig. 1 (inset) the exponential factor values resulted from fits were similar at each temperature, and the mean value of exponential factor (Gammov factor) was determined ($\beta = 0.14 \pm 0.03$ Å^{-1}). This value well agree with that obtained so far for ET reactions in the nucleic acids or oligonucleotide systems (Murphy et al. 1993; Meade and Kayyem 1995; Kelley et al. 1997; Kelley and Barton 1999, and references cited therein). Remarkable, values of parameter β, which reflects both the distance scale of ET as well as insulating properties of the medium between donor and acceptor, vary from ≤ 0.1 to >1.4 Å^{-1}. This was estimated in the systems of fixed distance (Murphy et al. 1993; Meade and Kayyem 1995) or by varying the distance (Kelley and Barton 1999; and references cited therein), as well as in dependence on stacking interaction of reactants (Kelley et al. 1997).

Exponential dependence of the m^3B fluorescence decay rate on the number of phosphates in the polyphosphate bridge of m^3Bp_nG dinucleotides ($n = 2, 3, 4$; Scheme 1) suggests that ET is a major factor responsible for fluorescence quenching in the studied systems. These data indicate an important role of the polyphosphate bridge length (number of phosphates) in the long range ET in dinucleotides, as well as in oligonucleotides and nucleic acids, including their biological and technical applications.

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