Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Size effect on the optical properties of guanine nanostructures: a femtosecond to nanosecond study

Ying Hua, Pascale Changenet-Barret, Thomas Gustavsson, and Dimitra Markovitsi[1*]

CNRS, IRAMIS, SPAM, Laboratoire Francis Perrin, URA 2453, 91191 Gif-sur-Yvette, France

*Address correspondence to: dimitra.markovitsi@cea.fr

- Fits of the fluorescence decays
- Determination of fluorescence properties of dGMP and TMP mixtures from independent measurements

Fits of the fluorescence decays.

We fitted the fluorescence decays using three-exponential functions. $F(t) = \sum_{i=1}^{n} a_i \exp(\frac{-t}{\tau_i})$, where a_i and τ_i represent pre-exponential factors and time constants, respectively. The average lifetime was defined as: $\langle\tau\rangle = \sum a_i\tau_i$.

Table SI-1. Fitted parameters determined for the FU (0-80 ps) and TCSPC (0-10 ns) fluorescence decays of $d(TG_5T)_4$ at 360 nm; they were used to construct the plots in **Figure 5b**; the time constants in ps.

	a_1	τ_1	a_2	τ_2	a_3	τ_3	$\langle\tau\rangle$
FU	0.62	0.15	0.17	1.28	0.21	12.17	2.9
TCSPC	0.9967	15	0.0029	188	0.0004	1847	16.3

Table SI-2. Fitted parameters determined for the TCSPC fluorescence decays of G-quadruplexes at 450 nm. The corresponding fitted functions were used to construct the histograms in **Figure 6;** the time constants in ps.

	a_1	τ_1	a_2	τ_2	a_3	τ_3	$\langle\tau\rangle$
$d(TG_3T)_4$	0.887	14	0.106	81	0.007	624	25.7
$d(TG_4T)_4$	0.959	19	0.036	164	0.005	1451	30.9
$d(TG_5T)_4$	0.954	19	0.037	164	0.009	1453	36.8

Determination of fluorescence properties of dGMP and TMP mixtures from independent measurements

The fluorescence spectra and florescence anisotropies of dGMP and TMP mixtures shown, in Figures 3 and 7, were determined using the dGMP and TMP properties determined previously, according to equations below..

a) fluorescence spectra:

$$F(\lambda) = \sum_i (1 - 10^{-x_i \times A_Q}) \times \phi_i \times \frac{F_i(\lambda)}{\int F_i\,(\lambda) \times d\lambda}$$

$$x_i = \frac{n_i \times \epsilon_i}{\sum_i n_i \times \epsilon_i}$$

The subscripts *i* and *Q* denote, respectively, the mono-nucleotide i and the G-quadruplex. n_i : molar fraction of mono-nucleotide *i* in the G-quaduplex; A_Q is the absorbance and ϵ_i the molar extinction coefficient at the excitation wavelength; ϕ_i is the fluorescence quantum yield; F_i represents the normalized fluorescence spectrum; λ : emission wavelength.

b) fluorescence anisotropies at the emission wavelength λ_{em}:

$$r(\lambda, t) = \frac{\sum_i (1 - 10^{-x_i \times A_Q}) \times \phi_i \times \frac{F_i(\lambda_{em})}{\int F_i\,(\lambda) \times d\lambda} \times \frac{I_i(\lambda_{em}, t)}{\int I_i\,(\lambda_{em}, t) \times dt} \times r_i(\lambda_{em}, t)}{\sum_i (1 - 10^{-x_i \times A_Q}) \times \phi_i \times \frac{F_i(\lambda_{em})}{\int F_i\,(\lambda) \times d\lambda} \times \frac{I_i(\lambda_{em}, t)}{\int I_i\,(\lambda_{em}, t) \times dt}}$$

$\mathrm{I_i(\lambda_{em}, t)}$ represents the fluorescence intensity of mononucleotide I recorded at time *t* and r_i the fluorescence decay .