

Steady-State Spectroscopic and Fluorescence Lifetime Measurements of New Two-Photon Absorbing Fluorene Derivatives

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Steady-state excitation anisotropy, lifetimes, and time-resolved emission spectra of new 2-photon absorbing fluorene derivatives were measured in aprotic solvents at room temperature. Excitation anisotropy spectra in viscous silicon oil allowed the determination of the spectral position of three electronic transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$ (S_i , $i = 1, 2, 3$ are the singlet electronic states) and the angles ($\approx 30^\circ$) between absorption $S_0 \rightarrow S_1$ and emission $S_1 \rightarrow S_0$ dipole moments for the first electronic transition. Solvate relaxation processes in the first excited state of the investigated fluorene molecules affect the lifetimes of these states, τ_1 , so that experimental values of τ_1 do not correspond to those calculated by Strickler and Berg theory. The influence of the molecular concentration on the fluorescence quantum yields and τ_1 have been investigated.

KEY WORDS: Steady-state spectroscopy; fluorescence lifetime; anisotropy.

INTRODUCTION

Photophysical properties of fluorene-based derivatives have been the subject of intensive investigations because of their potential application in a number of emerging technologies. Depending on the molecular structure, they can possess efficient photoconducting properties [1], high fluorescence quantum yields in liquid and solid (polymeric) media [2–4], thermal- and photostability, which make them applicable to electronic and photonic devices such as field-effect transistors [5–6] and light-emitting diodes [7–10]. Fluorene-based organic materials exhibit various non-linear optical

properties, including optical limiting behavior [11] and efficient 2-photon absorption (TPA) processes [12,13], which are important for application in 2-photon fluorescence imaging [14], 2-photon photodynamic cancer therapy, [15], and 2-photon microfabrication [16].

We recently reported the synthesis of several new diphenylamino-substituted fluorene derivatives as efficient 2-photon absorbing dyes [12,13], along with a cursory investigation of their steady-state spectroscopic parameters [4]. In this paper we investigated (7-benzothiazol-2-yl-9,9-didecylfluoren-2-yl)-diphenylamine (**1**), 9,9-didecyl-2, 7-bis-(*N,N*-diphenylamino) fluorene (**2**), and {4-[2-(7-diphenylamino-9,9-diethylfluoren-2-yl)-vinyl]phenyl} phosphoric acid diethyl ester (**3**) (Fig. 1). To better understand their photophysical properties and their potential for a number of applications, a comprehensive study was conducted for these compounds, including fluorescence lifetime, τ_1 , time-resolved emission spectra (TRES), and concentration dependencies of quantum yields and τ_1 .

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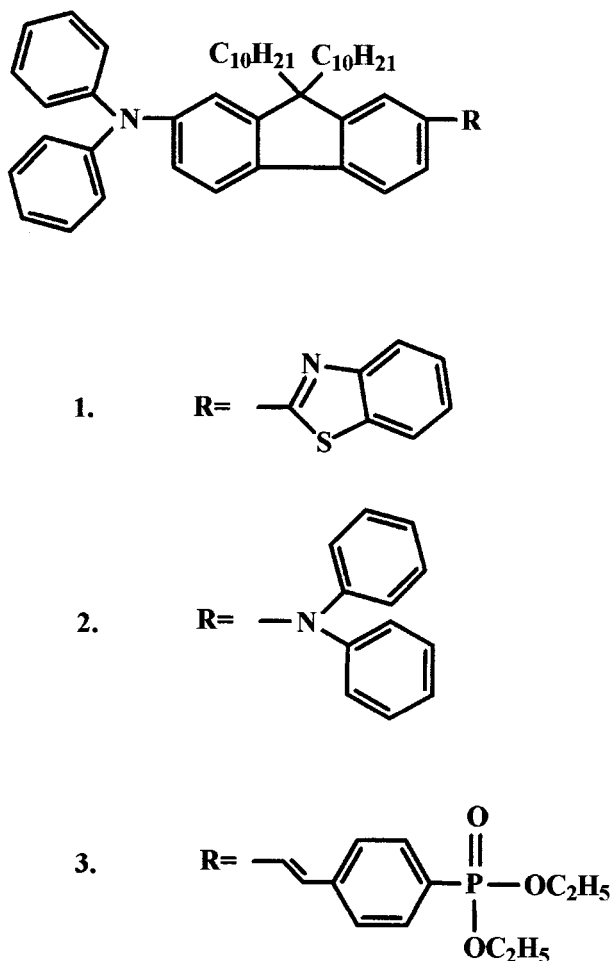


Fig. 1. Chemical structures of the fluorene compounds 1–3.

EXPERIMENTAL

The synthesis of (7-benzothiazol-2-yl)-9,9-didecylfluorene-2-yl)-diphenylamine (1), 9,9-didecyl-2,7-bis-(*N,N*-diphenylamino) fluorene (2), and {4-[2-(7-diphenylamino-9,9-diethylfluorene-2-yl)vinyl]phenyl} phosphoric acid diethyl ester (3) were previously described [12,13]. Steady-state spectral properties and fluorescence lifetimes of 1–3 were measured in hexane, THF, CH_2Cl_2 , acetonitrile (ACN), and silicon oil (viscosity ~ 200 cP at 25°C) with concentration $\leq 2 \times 10^{-6}$ M at room temperature in 10-mM quartz cuvettes.

Absorption spectra were obtained using a Cary-3 UV-visible spectrophotometer. Steady-state excitation anisotropy spectra were measured with a PTI Quantamaster spectrofluorimeter under 90° excitation in T-format method [17]. TRES and fluorescence lifetimes were obtained with a PTI Timemaster system with strobe photomultiplier tube and 600-ps laser pulse excitation, tun-

able in the spectral region 370–400 nm (GL 302 dye laser, pumped by GL 3300 nitrogen laser with 10-Hz repetition rate). The time resolution of this system was determined by the PTI Timemaster software and reached 0.1 ns. This was confirmed using the picosecond fluorescence lifetime standard 4-*N,N*-dimethylamino-4'-bromostilbene in cyclohexane at room temperature [17]. Fluorescence quantum yields, Φ , were measured by a standard method [17], relative to rhodamine 6G in ethanol ($\Phi \approx 0.94$) [18]. Absorption spectra, quantum yields, and fluorescence lifetimes were measured at the different concentrations of the fluorene molecules (up to 5×10^{-3} M) in CH_2Cl_2 in a 0.1-mm quartz cuvette. Fluorescence measurements (quantum yield and lifetimes) for high-concentration solutions were made in the near 0° angle excitation geometry (angle between surface of the cuvette and excitation direction). This geometry minimizes the influence of the reabsorption effects at high concentration.

RESULTS AND DISCUSSION

The absorption spectra for fluorene derivatives 1–3 in hexane, THF, ACN, and silicon oil are presented in Fig. 2–4 (curves 1–4). The absorption spectra exhibited weak dependencies on the solvent polarity, Δf [19], and was mainly determined by the molecular electronic structure. To determine the nature of the absorption bands, excitation anisotropy spectra of 1–3 were recorded in viscous silicon oil (Fig. 2–4, curve 5) [17]. For these curves, a constant value of anisotropy, τ_0 , for excitation in the spectral range $\lambda_{\text{exc}} \approx 350$ –400 nm was observed,

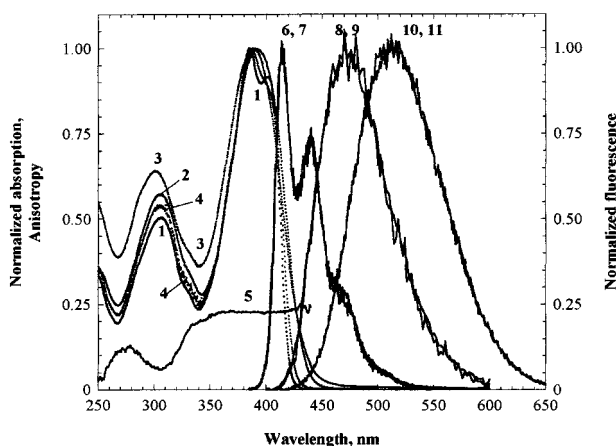


Fig. 2. Normalized absorption spectra (1–4), excitation anisotropy (5), and TRES for 0-ns delays (6, 8, 10) and 5-ns delays (7, 9, 11) for compound 1 in silicon oil (4, 5), hexane (1, 6, 7), THF (2, 8, 9), and ACN (3, 10, 11).

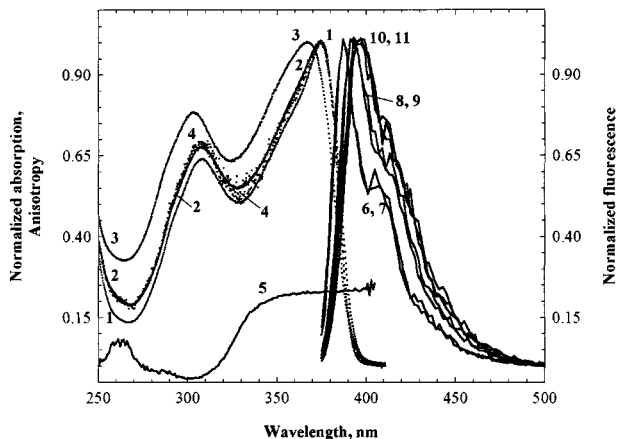


Fig. 3. Normalized absorption spectra (1–4), excitation anisotropy (5), and TRES for 0-ns delays (6, 8, 10) and 5-ns delays (7, 9, 11) for compound **2** in silicon oil (4, 5), hexane (1, 6, 7), THF (2, 8, 9), and ACN (3, 10, 11).

corresponding to the first electronic transition $S_0 \rightarrow S_1$ (S_1 , $i = 1, 2, 3$ are the singlet electronic states of the fluorene molecules). The minimum of the anisotropy value near $\lambda_{\text{exc}} \approx 300\text{--}310$ nm corresponded to the position of the second $S_0 \rightarrow S_2$ electronic transition and the next maximum near $\lambda_{\text{exc}} \approx 260\text{--}280$ nm corresponded to the third transition $S_0 \rightarrow S_3$.

The time-resolved emission spectra for compounds **1–3** in hexane, THF, and ACN are presented in Fig. 2–4 for various nanosecond delays: 0 ns (curves 6, 8, 10) and 5 ns (curves (7, 9, 11)). No differences in the fluorescence spectra for these two delays were observed for the three compounds within the limits of experimental accuracy. This means that all relaxation processes in the first excited

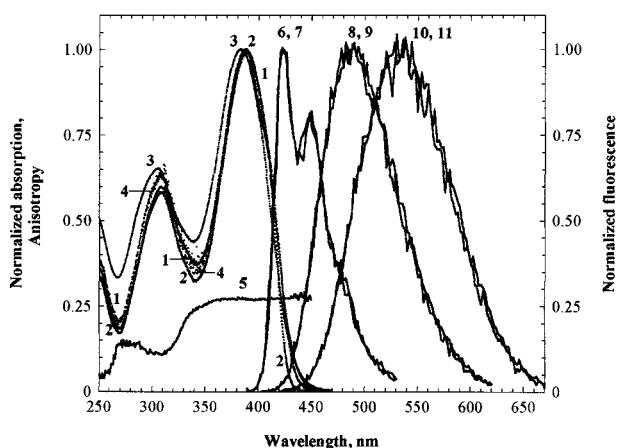


Fig. 4. Normalized absorption spectra (1–4), excitation anisotropy (5), and TRES for 0-ns delays (6, 8, 10) and 5-ns delays (7, 9, 11) for compound **3** in silicon oil (4, 5), hexane (1, 6, 7), THF (2, 8, 9), and ACN (3, 10, 11).

state S_1 , including the correlation times of solvent relaxation, τ_R [17], did not exceed the time resolution of the system (i.e., $\tau_R < 0.1$ ns).

In contrast to absorption, fluorescence spectra for nonsymmetrical compounds **1** and **3** exhibited strong dependencies on the orientation polarizability or solvent polarity, Δf . A linear correlation between the Stoke's shifts of emission spectra and Δf , predicted by the Lippert equation [7,19], indicated the absence of specific solute-solvent interactions for **1** and **3** in aprotic solvents [4]. In the nonpolar solvent hexane, the fluorene derivatives exhibited well-resolved vibrational structures. This is typical for molecules with conjugated π -systems due to minor energy stabilization of molecule's ground and first excited electronic states by general solvent interactions. In polar solvents the vibronic transitions overlap due to solvent relaxation processes in the first excited state [17] and, as a rule, broad spectra with indistinct features are observed.

Emission spectra for compound **2** exhibited only a small Stoke's shift and a weak dependence on the solvent polarity, typical for symmetrically substituted fluorophores in aprotic solvents. The extinction coefficients (molar absorptivities), ϵ^{max} , presented in Table I, for **1–3** in four aprotic solvents are essentially independent of solvent with the exception of **1** in CH_2Cl_2 .

Experimental values of the fluorescence lifetimes, τ_1 , for compounds **1–3** in five solvents are presented in Table I. Evident from these data, τ_1 did not exceed 3.25 ns. Rotational movements of the molecules in solution during the emission lifetime strongly decrease fluorescence anisotropy. Rotational correlation time, θ , for **1–3** in liquid solutions can be approximated from the equation [17]:

$$\theta = \eta V/kT \quad (1)$$

where η is the solvent viscosity, V is volume of the rotating molecule, k is Boltzman's constant, and T is temperature in Kelvin. It can be shown from (1) that values of θ for **1–3** in silicon oil (a viscous solvent) at room temperature are $\theta \geq 30\text{--}50$ ns. Thus, the fluorene molecules **1–3** in silicon oil did not rotate during their fluorescence lifetime ($\tau_1 \ll \theta$). Further, the maximum value of the anisotropy, r^{max} , should be equal to 0.4 in the case of parallel orientation of the dipole moments in absorption $S_0 \rightarrow S_1$ and emission $S_1 \rightarrow S_0$. However, the experimental values of r^{max} for compounds **1–3** in the main absorption band were constant and did not exceed 0.3 (see Figs. 2–4, curve 5). This can be explained by different orientations of the absorption and emission dipole moments, owing to the different electronic distribution in the ground and first excited states of the mole-

Table I. Photophysical Parameters for Compounds **1**, **2** and **3**

	Compound 1					Compound 2					Compound 3					
	Fluorene	ACN	CH ₂ Cl ₂	THF	Hexane	Silicon Oil	ACN	CH ₂ Cl ₂	THF	Hexane	Silicon Oil	ACN	CH ₂ Cl ₂	THF	Hexane	Silicon Oil
Φ	0.9 ± 0.08	0.9 ± 0.1	0.55 ± 0.05	0.7 ± 0.08	–	–	0.7 ± 0.1	0.15 ± 0.02	0.5 ± 0.08	0.4 ± 0.05	–	0.9 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	0.6 ± 0.05	–
τ_R , ns	3.0 ± 1.0	3.7 ± 0.5	2.1 ± 0.5	2.2 ± 0.4	–	–	2.7 ± 1.0	2.0 ± 0.4	2.9 ± 0.5	2.1 ± 0.5	–	3.1 ± 1.0	2.1 ± 0.5	2.7 ± 0.5	1.5 ± 0.4	–
τ_1^{cal} , ns	2.7 ± 0.5	3.3 ± 0.5	1.3 ± 0.3	1.5 ± 0.3	–	–	1.9 ± 0.5	0.3 ± 0.06	1.4 ± 0.3	0.8 ± 0.2	–	2.8 ± 1.0	1.7 ± 0.4	2.4 ± 0.5	0.9 ± 0.3	–
τ_1 , ns	3.25 ± 0.15	2.4 ± 0.15	2.2 ± 0.1	1.25 ± 0.05	1.7 ± 0.15	–	1.15 ± 0.1	1.0 ± 0.2	1.0 ± 0.15	0.95 ± 0.2	1.07 ± 0.15	2.95 ± 0.15	2.5 ± 0.15	2.1 ± 0.15	1.25 ± 0.08	1.5 ± 0.15
$\epsilon^{\text{max}} * 10^{-1}$	68 ± 7	38 ± 4	62 ± 7	53 ± 5	–	–	38 ± 4	37 ± 4	30 ± 3	44 ± 5	–	62 ± 7	65 ± 7	58 ± 6	75 ± 8	–
$M^{-1} * \text{cm}^{-1}$	7	4	7	5	–	–	4	4	3	5	–	7	7	6	8	–
$\tau_1(\text{C})$, ns	–	2.5 ± 0.2	–	–	–	–	1.0 ± 0.15	–	–	–	–	2.3 ± 0.1	–	–	–	–
C, M	–	5 * 10 ⁻³	–	–	–	–	5 * 10 ⁻³	–	–	–	–	3 * 10 ⁻³	–	–	–	–
$\Phi(\text{C}_1)$	–	≈ 2	–	–	–	–	≈ 3	–	–	–	–	≈ 2.5	–	–	–	–
$\Phi(\text{C}_2)$	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
C ₁ , M	–	2.3 * 10 ⁻⁶	–	–	–	–	2.7 * 10 ⁻⁶	–	–	–	–	2.6 * 10 ⁻⁶	–	–	–	–
C ₂ , M	–	3.4 * 10 ⁻³	–	–	–	–	5.7 * 10 ⁻³	–	–	–	–	3 * 10 ⁻³	–	–	–	–

cule [20]. It is known that the fluorene derivatives exhibit a considerable change in the absolute values of the dipole moments upon excitation [19]. Thus a change in the orientation of their emission dipole moments in S₁ can be expected along with a decrease in r^{max}. The angle between these dipole moments, α , was estimated from the formula [17]:

$$r^{\text{max}} = (3\cos^2 \alpha - 1)/5$$

For compounds **1–3** $\alpha \approx 30^\circ$ in the nonpolar silicon oil.

Fluorene molecules **1–3** in low-viscosity non-polar solvents at room temperature (e.g., hexane) exhibited a considerable decrease of anisotropy owing to their fast rotation in the first excited state S₁ during their fluorescence lifetime. As can be seen in Fig. 5 (curve 1), the value of anisotropy in hexane did not exceed 0.05. For ACN (curve 2), the anisotropy was lower and more complicated (especially for non-symmetrical compounds **1** and **3**). Considerable rearrangement of the solvate cage occurred after excitation for non-symmetrical fluorene molecules in polar solvents [19], reflected in the large Stoke's shifts. We assume that this rearrangement is also responsible for a change of the orientation of emission dipole moments and decrease in r^{max}.

Quantum yields, Φ , natural radiative lifetimes, τ_R (calculated by Bircks and Dyson formula [21], which is based on Strickler and Berg theory [22]), and calculated fluorescence lifetimes $\tau_1^{\text{cal}} = \tau_R^{\text{cal}} \Phi$, are also presented in

Table I. The observed fluorescence decays for **1–3** in all solvents that were investigated correspond to a single exponential process with typical goodness-of-fit parameters $\chi^2 \leq 1.1$. The experimental values of the fluorescence lifetimes, τ_1 , were in reasonable agreement with calculated values τ_1^{cal} only for nonpolar solvent (hexane).

The values of τ_1 and τ_1^{cal} for polar solvents differ by a factor of up to 3 (e.g., **2** in CH₂Cl₂) with the exceptions of **1** and **3** in ACN. This suggests that the solvent relaxation of the fluorene molecules in the first excited state (for polar solvents) may shift molecular electronic levels, so the fluorescence spectrum of this new electronic structure does not correspond to the observed absorption S₀ → S₁ (even for symmetrical compound **2**). After excitation, there is a considerable change in the excited state dipole moment (hence electronic distribution) of the fluorene derivative. The solvent then reorients around this new electronic distribution, resulting in a new excited state energy level lower in energy than the original S₁. The observed fluorescence then corresponds to this new level, not the original excited state. In Strickler and Berg theory it is assumed that fluorescence occurs from the original excited state and the theory does not take into account solvent reorientation and subsequent formation of a new lower-energy excited state. Hence, the relationships between absorption and emission spectra may be more complicated than simply following Strickler and Berg theory and τ_1 does not correspond to τ_1^{cal} . These results

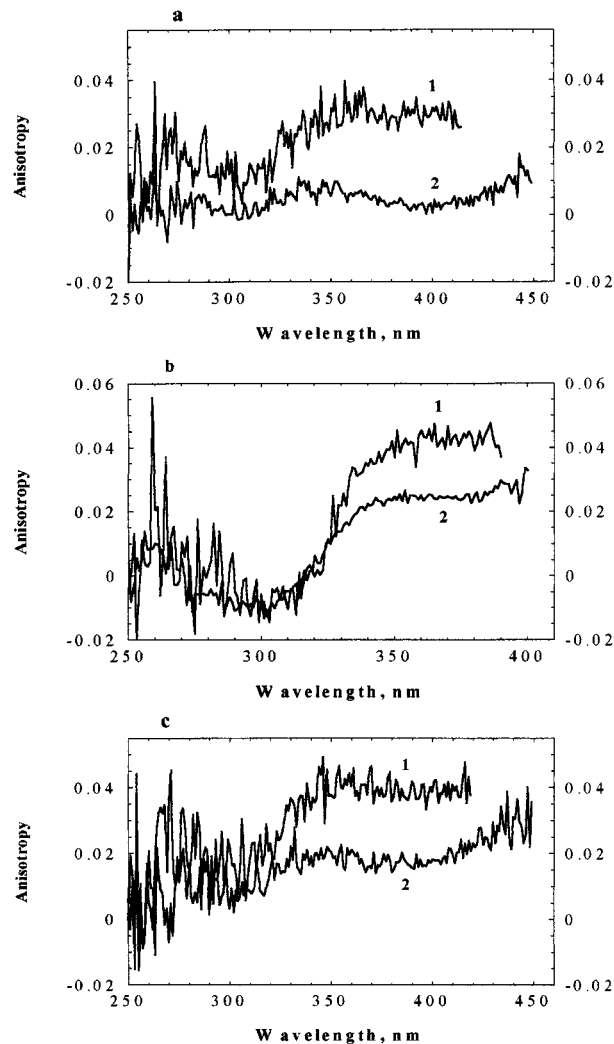


Fig. 5. Excitation anisotropy for compounds **1** (a), **2** (b), and **3** (c) in hexane (curve 1) and ACN (curve 2).

indicate the importance of considering the medium on fluorescence properties for the fluorene derivatives.

The relations $\Phi(C_1)/\Phi(C_2)$ between fluorescence quantum yields for low (C_1) and high (C_2) concentration solutions of **1–3** in CH_2Cl_2 and their observed lifetimes, $\tau_1(C)$, of the first excited states are also presented in Table I. From these data, it can be seen that the lifetimes of **1–3** were independent of concentration, C , up to 5×10^{-3} M. However, at higher concentrations the values of the quantum yields decreased dramatically (2–3 times), suggestive of the formation of non-fluorescent aggregates of the fluorene molecules (e.g., dimers) for **1–3** in CH_2Cl_2 . These aggregates absorbed a significant amount of excitation energy without emission, which led to a decrease in quantum efficiency. No evidence of a decrease in lifetime τ_1 , owing to collisional quenching of monomer molecules

in high-concentration solutions, was found at concentrations $C \leq 5 \times 10^{-3}$ M. It is interesting to note that the absorption spectra of compounds **1–3** (in CH_2Cl_2) for concentrated solutions were absolutely the same as for dilute solutions. That means the monomeric and aggregated fluorene molecules exhibited the same absorption behavior over this range of concentrations. The same effect was observed for rhodamine 6G in ethylene glycol at concentrations $C \leq 10^{-2}$ M [23].

CONCLUSIONS

Steady-state absorption, excitation anisotropy, and TRES spectra for new TPA fluorene compounds **1–3** were measured in aprotic solvents at room temperature. Excitation anisotropy spectra for **1–3** in viscous silicon oil allowed the determination of the spectral position of three electronic transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$ and the angles ($\approx 30^\circ$) between absorption $S_0 \rightarrow S_1$ and emission $S_1 \rightarrow S_0$ dipole moments for the first electronic transitions. TRES of **1–3** in all the solvents that were investigated were independent of nanosecond time delays and exhibited a strong dependence on solvent polarity for non-symmetrical compounds **1** and **3**.

The values of lifetimes, τ_1 , for **1–3** in polar aprotic solvents, which were experimentally measured and calculated by the Bircks and Dyson formula, did not correspond to each other, owing to a significant change of the electronic structures of the fluorene molecules after solvate relaxation processes. Decreases in the fluorescence quantum yields for high-concentration solutions of **1–3** in CH_2Cl_2 ($C \leq 5 \times 10^{-3}$ M) were not connected with collisional quenching of the fluorene molecules (because the lifetimes were the same at high and low concentrations) and can be explained by the presence of molecular nonradiative aggregates.

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