PCCP

Accepted Manuscript

PCCP

RSCPublishing

ARTICLE

Excited-state properties of fluorenones: influence of substituents, solvent and macrocyclic encapsulation†

Cite this: DOI: 10.1039/x0xx00000x

Received xxth January 2014,
Accepted xxth January 2014

DOI: 10.1039/x0xx00000x

www.rsc.org/pccp

Indrajit Ghosh,[a] Arindam Mukhopadhyay,[b] Apurba Lal Koner,[a] Subhas Samanta,[b] Werner M. Nau*[a] and Jarugu Narasimha Moorthy*[b]

Abstract: A comprehensive investigation of the photophysics of a broad set of fluorenones substituted with methoxy groups at different positions brings out the importance of the location of substituents on the fluorenone core in modulating fluorescence and radiationless deactivation by way of modification of the singlet-excited state energy and its character. While the substituents at para positions are found to affect neither the fluorescence quantum yield nor the lifetime, those at meta positions are found to significantly modify the latter. A cumulative effect is observed for the substituents in that the nonradiative decay (k_{nr}) becomes progressively dominant with increasing number of meta-methoxy substituents. For example, the trimethoxy substitution in 2,4,7-trimethoxyfluorenone (**8**) is found to increase k_{nr} by ca. 30 fold relative to that of the parent fluorenone (**1**) in a polar aprotic solvent such as acetonitrile. The predominance of nonradiative decay (k_{nr}) is rationalized from stabilization of the singlet-excited state via partial charge transfer from meta-methoxy substituents to the carbonyl group. Accordingly, a nice correlation is observed for the nonradiative (k_{nr}) rate constants versus singlet-excitation energies derived from fluorescence emission maxima of all fluorenones in acetonitrile. The macrocyclic host cucurbit[7]uril (CB7) is found to not only enhance the fluorescence of the parent fluorenone (**1**) significantly, but also increase the singlet lifetime considerably. Based on the changes observed in the absorption spectra and the lifetimes determined, a 1:1 host–guest complex has been proposed with CB7. The fluorescence lifetime observed in the presence of CB7 suggests that the hydrophobic fluorenone (**1**) can be employed as a probe to report on a polar microenvironment shielded from hydrogen bonding interactions in a polar protic solvent.

---

[a] *Jacobs University Bremen, Campus Ring 1, D-28759 Bremen, Germany. E-mail: w.nau@jacobs-university.de*

[b] *Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India.*

E-mail: moorthy@iitk.ac.in

†Electronic Supplementary Information (ESI) available: The UV-vis absorption and fluorescence emission spectra for all fluorenones **1-9** in different solvents, and the details of determination of ground- and excited-state dipole moments of fluorenones **2** and **3**. See DOI: 10.1039/x0xx00000x

1 Introduction

The understanding of how structural modifications and environmental factors such as medium, temperature, etc. influence the excited state properties constitutes a fundamental goal in photochemistry. In this regard, benzophenone has served as a prototype carbonyl compound in establishing the photochemistry of organic compounds with n,π* excited state in general and ketones in particular. In contrast, its cyclic analog, namely fluorenone **1** (Fig. 1), is renowned for its excited state π,π* character and solvent-dependent photophysical properties that include fluorescence quantum yield, fluorescence lifetime and rates of nonradiative decay and intersystem crossing.[1-5] In general, the essence of a number of comprehensive investigations that have focused on deciphering the photophysical properties of fluorenone and several of its derivatives is the following: i) the lowest energy singlet-excited S_1 state is of π,π* character in a polar solvent and n,π* in a nonpolar solvent, while the triplet-excited T_1 and T_2 states of all

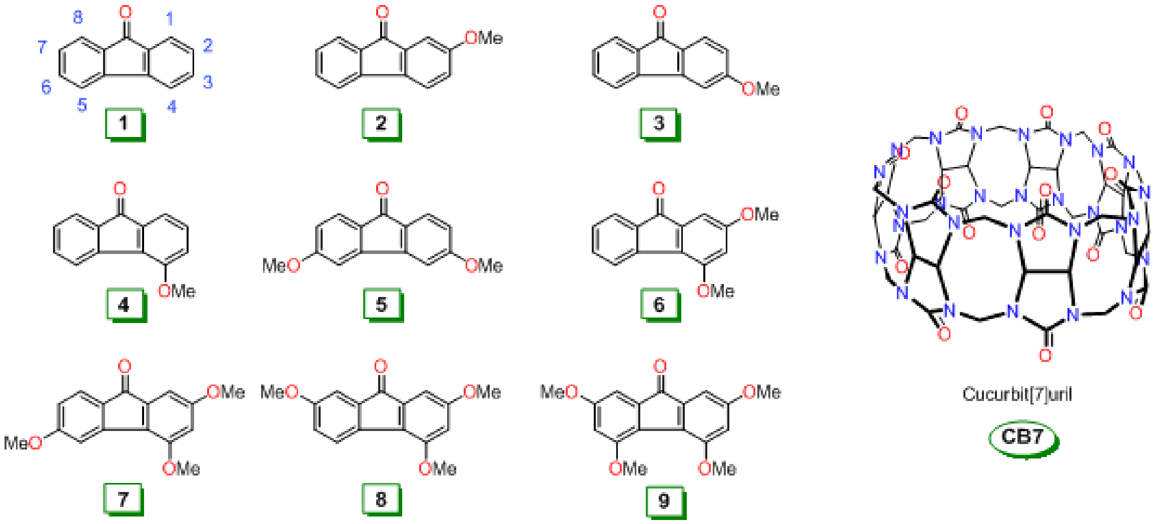


Fig. 1 The structures of fluorenones **1-9** and cucurbit[7]uril.

fluorenones are of π,π* character; ii) the triplet-excited T_3 state is of n,π* character; iii) the dominating process for photoexcited fluorenones in nonpolar and moderately polar solvents is, in general, exothermic intersystem crossing (isc) from S_1 to the proximate T_1 and T_2 states with respectable quantum yields of triplet formation; iv) polar aprotic as well as polar protic solvents raise the energy of T_3 such that isc from S_1 becomes difficult leading to radiative (fluorescence) and nonradiative relaxation as chief pathways of S_1 deactivation; v) polar protic solvents quench fluorescence and promote internal conversion. Furthermore, the hydrogen bond dynamics of the parent fluorenone have been found to be influenced by photoexcitation; the vibrational energy relaxation of fluorenones in alcohols has been shown occur via hydrogen bonding, as revealed by femtosecond IR spectroscopy.[6] From DFT calculations on site-specific solvation dynamics of photoexcited fluorenone in methanol, the intermolecular hydrogen bonding between methanol and fluorenone has been suggested to be strengthened in the excited state.[7] Hydrogen bonding has been surmised to act as an accepting mode of radiationless deactivation for electron-rich fluorenones. Thus, internal conversion (ic) from S_1 has been shown to be facilitated by H-bond strengthening in the excited state.[4]

Insofar as the diversity in terms of substituted fluorenones investigated is concerned, a number of derivatives with substituents located at all positions of the fluorenone nucleus have been examined to gain insights into the substituent effects on excited-state deactivation mechanisms.[3,8-14] While electron-withdrawing groups have been shown to increase isc, electron-donating substituents have been found to promote internal conversion.[3,11] Halogen substitution has been shown to lead to heavy atom effect.[8] For 2-, 3- and 4-aminofluorenones, ic from S_1 state has been shown to be accelerated in a polar protic solvent such as ethanol.[13] A notable solvent deuterium isotope effect has been reported for the internal conversion rate constant of 4-aminofluorenone.[10] In a series of 2-substituted fluorenones, electron density on the carbonyl oxygen has been shown to influence the alcohol quenching rates of the singlet-excited states.[4] Although the effects of substituents on isc and ic have been investigated thoroughly,[3,11,13] the knowledge of how substituents at different positions of the fluorenone nucleus, i.e., ortho/meta/para with respect to the carbonyl group, influence photophysical processes is intriguingly obscure except for amino–substituted derivatives;[11,13,14] in the latter, however, the amino substituents may engage in electron-transfer mechanisms to shroud generalizations as to the effects of substituents at different positions.

In the backdrop of the foregoing literature, a comprehensive analysis of the photophysical processes of a broad set of fluorenones substituted with an electron-donating substituent such as the methoxy group deemed compelling to establish how its location at different positions of the fluorenone nucleus influences the singlet-excited state deactivation via fluorescence and internal conversion. As the methoxy substitution at meta and para positions of the carbonyl group in 2- and 3-methoxy-9-fluorenones (**2** and **3**) should be expected to exert mesomeric effects to varying degrees, the photophysical processes of the corresponding excited states should be expected a priori to be influenced accordingly. In particular, we wondered if cumulative effects would be discerned in substrates with multiple substitution of methoxy groups; a better understanding of the photophysical properties of fluorenone and its derivatives is important in view of their relevance, for example, in the development of sensors,[15] electroluminescence of polyfluorenes,[16] probing electron transfer dynamics in protic media,[17] etc. Thus, we sought to delineate and contrast the effect of methoxy substituent(s) at different positions of the fluorenone on the radiative and nonradiative deactivation pathways by steady-state as well as time-resolved fluorescence spectroscopic investigations of a series of fluorenones **1-9** shown in Fig. 1. Further, investigation of the extent to which macrocyclic encapsulating host systems such as cucurbiturils[18-22] influence the excited-state dynamics in a polar protic solvent appeared compelling in light of the fact that fluorenones have been employed as model candidates to investigate deactivation of excited states.[23] Herein, we report the results of our comprehensive investigations on the dynamics of the singlet-excited state decay in a broad set of methoxy–substituted fluorenones **1-9**, which emphasize the importance of the location of the substituents. Further, we show that encapsulation of the parent fluorenone **1** in cucurbit[7]uril (CB7) leads to enhancement of fluorescence as well as an increase in the singlet-excited state lifetime significantly via protection from site-specific hydrogen bonding in aqueous medium. The results suggest that fluorenone may serve as a promising probe of polar aprotic environments based on fluorescence lifetimes.

2 Results and discussion

2.1 Absorption and fluorescence properties of fluorenones 1-9

In Fig. 2 are shown the absorption and fluorescence spectra of monomethoxy–susbtituted fluorenones **1-4** in acetonitrile; the concentrations were ca. 100 μM. As can be seen, the absorption spectra are characterized by a broad band in the region between 340–520 nm and a strong structured band in the short-wavelength region with high molar absorptivity. What is noticeable is that the parent fluorenone **1** and 3-methoxyfluorenone **3** show similar absorption features, while 2- and 4-methoxyfluorenones, i.e., **2** and **4**, likewise exhibit a broad absorption band with almost identical molar absorptivities.

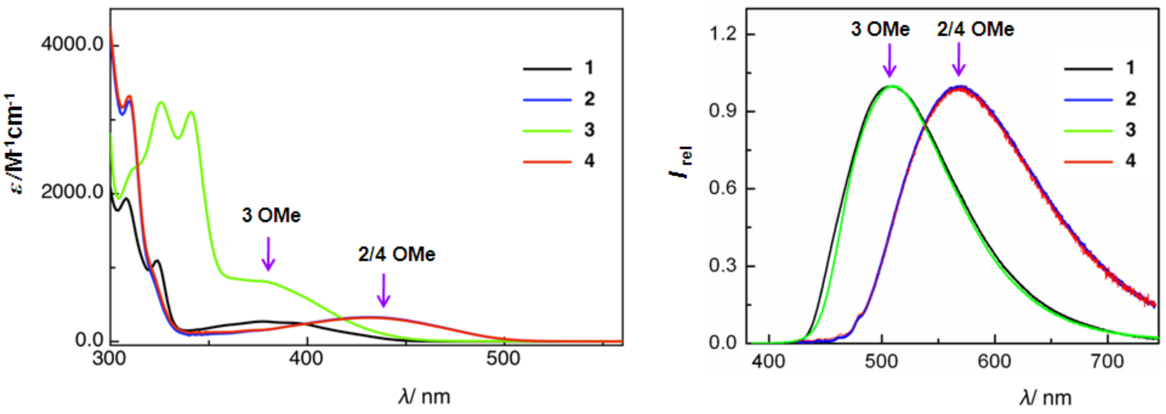


Fig. 2 Absorption (left) and fluorescence emission spectra (right) of fluorenone **1** and its methoxy–substituted derivatives **2-4** in acetonitrile. The emission spectra of fluorenones **1-4** were recorded by exciting the samples at their long wavelength absorption maxima, cf. Table 1. Note that the optical spectra of **2** and **4** are virtually identical.

While dimethoxy–substituted 3,6-dimethoxyfluorenone **5** exhibited absorption similar to those of **1** and **3**, 2,4-dimethoxyfluorenone **6** was found to show a highly red-shifted absorption maximum, cf. Table 1. Clearly, the substitution by a methoxy group at the 3 and 6 positions does not bring about any change, while a red shift in the absorption maximum is observed progressively for substitution at the 2, 4, 5 and 7 positions. Accordingly, one observes a shift in the absorption maximum from 432 nm to 504 nm on going from fluorenones **2** to **9** in acetonitrile (Figs. S1-S9, ESI†). A corresponding shift in the long-wavelength absorption maximum is also observed in a nonpolar cyclohexane solvent. For all fluorenones with the exception of **1**, the absorption maximum is found to be red shifted by 9-19 nm for change in the solvent from cyclohexane to acetonitrile (Table 1). Further, one observes that the effect of hydrogen bonding solvent is more for para-methoxy–substituted fluorenones than for meta-methoxy–substituted ones.

A considerable difference in the Stokes shift for the emission of fluorenones in nonpolar vs. polar and polar protic solvents is noteworthy. As shown in Table 1, ca. 2-fold difference is observed in the Stokes shift for the parent fluorenone **1** in cyclohexane vs. ethanol. Due to very low fluorescence quantum yields (< 0.01%), the emission spectra for **2** and **4** could not be recorded in ethanol. Otherwise, a comparison of the Stokes shifts for fluorenones **2-4** in cyclohexane and acetonitrile show that the differences are not as pronounced when compared to that observed for the parent fluorenone **1**. Respectable shifts observed in the emission maxima of all fluorenones in going from cyclohexane to acetonitrile suggest that the excited states have larger dipole moments than their corresponding ground states. It is noteworthy that solvent-induced shifts are less pronounced for **3** when compared to those observed for **2** and **4** amongst monomethoxy–substituted fluorenones. Insofar as the emission quantum yields are concerned, all fluorenones are weakly fluorescent. The quantum yield of the parent fluorenone **1** has been reported to be 2.7% in acetonitrile;[8] this value was indeed reproduced in our experiments.

Table 1 Photophysical Properties of Fluorenones **1-9**^{a}

		absorption		fluorescence					
fluorenone	solvent	λ_{max} (nm)	ε ($10^3\times$ $M^{-1}cm^{-1}$)	λ_{max} (nm)	Φ_f (%)	τ ^{b} (ns)	Stokes shift (nm)	k_r (10^6s^{-1})	k_{nr} (10^8s^{-1})
1	cyclohexane	382	0.28	463	0.04	0.4	81	1.00	25.00
	acetonitrile	377	0.26	507	2.70	17.8	130	1.52	0.55
	ethanol	379	0.26	553	0.09	1.9	174	0.46	5.15
2	cyclohexane	421	0.38	518	3.40	9.9	97	3.40	0.97
	acetonitrile	432	0.33	568	0.18	1.8	136	1.00	4.50
	ethanol	433	0.33	–^{c}	< 0.01	–^{c}	–^{c}	–^{c}	–^{c}
3	cyclohexane	365	0.68	472	0.07	5.3	107	0.13	1.87
	acetonitrile	379	0.78	510	3.40	14.0	131	2.44	0.69
	ethanol	387	0.72	549	0.20	1.1	162	1.90	9.41
4	cyclohexane	420	0.35	518	3.40	10.7	98	3.18	0.90
	acetonitrile	432	0.32	568	0.17	1.8	136	0.94	5.52
	ethanol	432	0.29	–^{c}	< 0.01	–^{c}	–^{c}	–^{c}	–^{c}
5	cyclohexane	361	1.31	490	0.28	1.8	129	1.56	5.54
	acetonitrile	376	0.93	514	2.80	15.7	138	1.78	0.62
	ethanol	382	1.36	552	0.20	0.8	170	2.41	12.00
6	cyclohexane	446	0.80	537	2.60	5.8	91	4.50	1.69
	acetonitrile	455	0.85	592	0.12	0.9	137	1.40	11.60
	ethanol	455	0.78	–^{c}	< 0.01	–^{c}	–^{c}	–^{c}	–^{c}
7	cyclohexane	422	0.41	537	0.95	4.4	115	2.15	2.24
	acetonitrile	441	0.44	578	0.12	1.2	137	1.04	8.69
	ethanol	442	0.42	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}	–^{c}
8	cyclohexane	478	0.62	570	0.24	1.3	108	1.82	7.56
	acetonitrile	491	0.54	628	0.01	0.6^d	137	0.17	16.60
	ethanol	492^e	0.54	–^{c}	< 0.01	–^{c}	–^{c}	–^{c}	–^{c}
9	cyclohexane	489	1.25	585	0.08	0.8^d	96	1.00	12.50
	acetonitrile	504	1.23	–^{c}	< 0.01	–^{c}	–^{c}	–^{c}	–^{c}
	ethanol	506	1.09	–^{c}	< 0.01	–^{c}	–^{c}	–^{c}	–^{c}

[a] ε, Φ_f, τ, Stokes shift, k_r and k_{nr} refer to molar extinction coefficient, fluorescence quantum yield, fluorescence lifetime, the difference between the long-wavelength absorption λ_{max} and fluorescence emission λ_{max}, radiative rate constant and non-radiative rate constant. The accuracy of the values Φ_f and τ are estimated to be ± 10% and ± 3%, respectively. λ_{max} for UV and fluorescence are ±1 nm. [b] The fluorescence lifetimes were determined at the emission maxima. [c] The fluorescence quantum yield was too low. [d] The fluorescence decay was biexponential; the lifetime of the component with larger contribution to the emission was considered for k_r and k_{nr} calculations. [e] Broad shoulder with no clear maximum.

Using the parent fluorenone as a secondary standard, the fluorescence quantum yields determined for all other fluorenones **2-9** in the three different solvents, namely cyclohexane, acetonitrile and ethanol, are collected in Table 1. The quantum yield data in Table 1 reveal that fluorenones with methoxy substituent(s) at positions 3 and/or 6, i.e., **3** and **5**, exhibit quantum yields of fluorescence similar to that of the parent fluorenone **1**. In stark contrast, substitution at the 2, 4, 5 and 7 positions is found to diminish the quantum yield of fluorescence significantly, as revealed by the data in acetonitrile. Further, one observes an opposite trend for the fluorescence quantum yields and lifetimes of **1**, **3** and **5** on one hand and all others on the other hand when going from cyclohexane to acetonitrile. The fluorescence for **2**, **4**, and **6-9** in ethanol becomes too low for spectral acquisition. The fact that the quantum yields are affected only when the methoxy substituents are located at the 2, 4, 5 and 7 positions is clearly borne out from the data in Table 1.

2.2 Radiative (k_r) and nonradiative (k_{nr}) decay constants from time-resolved fluorescence studies

Time-resolved fluorescence measurements were carried out for all fluorenones **1-9** in cyclohexane, acetonitrile and ethanol. The fluorescence lifetime (τ) was determined for each of the fluorenones **1-9** using time-correlated single photon counting. Most decays were found to be single exponential in nature with the exception of a few, which were fitted to a biexponential decay function; for the latter, the lifetime component with larger contribution to the total emission was taken for the calculation of the radiative (k_r) and nonradiative rates (k_{nr}). The fluorescence decay traces for **1-8** in acetonitrile together with those for **1** in all three solvents are shown in Fig. 3. The rate constants thus derived are collected in Table 1.

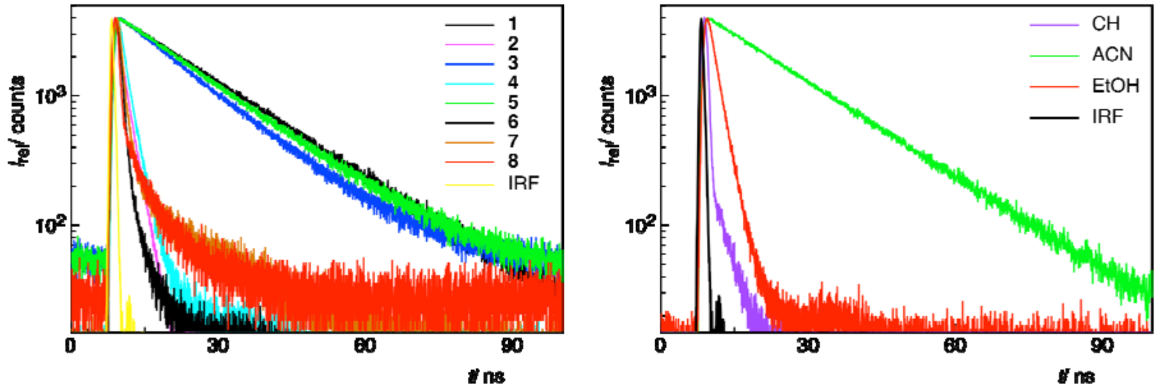


Fig. 3 Fluorescence lifetime decay traces (λ_{ex} = 373 nm) of fluorenones **1-8** in acetonitrile (left). Fluorescence lifetime decay traces (λ_{ex} = 373 nm) of the parent fluorenone **1** in cyclohexane (CH), acetonitrile (ACN), and ethanol (EtOH) (right).

2.3 Importance of the position(s) of substitution(s) of methoxy group(s) on the photophysical properties

To begin with, let us consider the absorption properties of monomethoxy–substituted fluorenones **2-4** relative to the absorption of parent fluorenone **1**. As noted earlier, the methoxy substitution at para position as in **3** brings about no change in the absorption relative to that of **1**. In contrast, the substitution at meta position as in **2** and **4** results in a red-shift of the long-wavelength absorption maximum. In a similar manner, substituents at 2, 4, 5 and 7 positions show cumulative effects such that the absorption maximum is significantly red-shifted down to 504 nm for fluorenone **9** in acetonitrile. Again, dimethoxy substitution as in **5** at the 3 and 6 positions does not influence the absorption maximum relative to that of the parent fluorenone **1**, cf. ESI†. As for the influence of substituents on the emission is concerned, corresponding shifts as those in the absorption spectra are observed on the emission maxima as well for changes in the positions of the substituents and increase in the number of the latter. Accordingly, fluorenones with substituents at the 2, 4, 5 and 7 positions are found to exhibit more red-shifted emission, cf. ESI†. Further, the quantum yields and fluorescence lifetimes for **1**, **3** and **5** increase when going from cyclohexane to acetonitrile, while they decrease for all other fluorenones, i.e., **2**, **4**, **6-9**, as mentioned earlier. Insofar as the nonradiative decay rates (k_{nr}s) are concerned, the values of k_{nr} for **1**, **3** and **5** in acetonitrile are approximately similar, which suggests that the substitution at positions 3 and 5 has no effect. For substitution at other positions, the values of k_{nr} are found to increase to the extent that the emission is too difficult to be observed as in the case of fluorenone **9**. Evidently, there appears to be a common factor that is responsible for the observed trends in the fluorescence quantum yields and nonradiative decay rates.

In our previous investigations on the photochemistry of 2-halobenzophenones, we noted that S_o-S_1 as well as T-T absorptions of meta-methoxy–substituted benzophenones do not follow the trends observed for the para–substituted analogs.[24] Indeed, it is well known that meta-methoxy substitution of acetophenone leads to stabilization of the π,π^* excited-state.[25-28] The intriguing transient T-T absorption and the triplet lifetime behavior of 2-bromobenzophenones were thus rationalized by us based on a partial intramolecular charge transfer involving transfer of some electron density from the electron-rich methoxy group at the meta position to the carbonyl group.[24] A similar consideration should apply here as well for the fluorenones examined to account for the observed shifts in the long wavelength absorption maxima with increasing methoxy substitution at the four meta postions of the fluorenone core; although resonance structures for fluorenones **2** and **4** do allow for extended conjugation, their contribution is less likely to be significant due to loss of aromaticity. Further, meta-methoxy substitution in acetophenones and benzophenones is known to stabilize π,π^* excited states and red shift the absorption maxima, despite the fact that there exists no possibility of resonance in these compounds.[24,26] It is noteworthy that intramolecular charge transfer (ICT) mechanism, facilitating rapid deactivation of the S_1 states, was proposed by Biczok *et al.* in an early investigation on photophysical properties of fluorenones.[3] The most recent investigations on substituted fluorenones by Neckers and co-workers also show that intramolecular charge transfer is the main mechanism of deactivation in 2,7-substituted fluorenones.[14] The electron-rich methoxy groups evidently stablilize the excited π,π* states more when located at the meta positions than at the para positions, as revealed by the shifts in the absorptions relative to the parent fluorenone **1**, e.g., **2**/**4** vs. **3**. Indeed, we have determined the ground and excited state dipole moments (μ_g and μ_e) for two representative meta- and para-methoxy–substituted fluorenones, that is, **2** and **3**, based on solvent-induced changes in the absorption and emission maxima, cf. ESI†. The ground state dipole moment for fluorenone **2** is found to be considerably less than that for **3** (1.06 vs. 4.33 D). However, the difference in the dipole moments of ground and excited states, i.e., $\mu_e – \mu_g$, is found to be significantly larger for **2** (1.76 D) than that for **3** (1.04 D). Thus, the ground state of **2** should be relatively more destabilized in a polar solvent. Accordingly, multiple substitution by methoxy groups at the meta positions of fluorenone should be expected to further lower the singlet-excited state energy by way of stabilization of the π,π* state. In line with this expectation, the tri- and tetramethoxy–substituted fluorenones **8** and **9** show highly red-shifted absorption bands, cf. ESI†.

A partial charge transfer from the meta-methoxy group to the π,π*-excited state should impart the carbonyl oxygen a surplus of charge such that it behaves as a better hydrogen-bond acceptor, Fig. 4. Based on the consideration of the stabilization of the excited state by electron-rich substituents at the meta position and the partial charge transfer that renders the carbonyl group more polar and the carbonyl oxygen more basic, we may now rationalize the fluorescence quantum yields, fluorescence lifetime data and nonradiative decay rates for all fluorenones **1-9** in Table 1. For fluorenones **3** and **5**, the methoxy substituent(s) at the para position(s) evidently does(do) not modify the excited-state character noticeably relative to that of the unsubstituted fluorenone **1**, and they exhibit similar quantum yields of fluorescence as well as monoexponential lifetime decays in a polar solvent such as acetonitrile in which the isc from S_1 to T_3 is not favorable, cf. Fig. 4. For substitution at the meta positions, the fluorescence quantum yields and the lifetimes drop. In these cases, the significantly polar singlet-excited π,π* state with partial charge transfer character is expected to be stabilized more in polar solvents, while the triplet n,π* state gets raised in energy (Fig. 4). Consequently, the isc should become less efficient in view of the fact that the transition is between electronic states of same character, i.e., π,π*. Indeed, it has been reported for 2-methoxyfluorenone that the T_3(n,π*) state appears to be higher in energy than the S_1(π,π*) state such that thermally-activated isc does not occur.[3] As the energy of S_1 becomes lower with stabilization of the π,π* state in a polar solvent, nonradiative decay is expected to become prominent over the radiative decay via fluorescence emission; the fact that the enhancement of vibrational coupling increases internal conversion has long been pointed out for fluorenones.[11,13] This trend is clearly seen to manifest itself in the quantum yields of fluorescence for multiply-substituted methoxy fluorenones, cf. Table 1. As mentioned earlier,

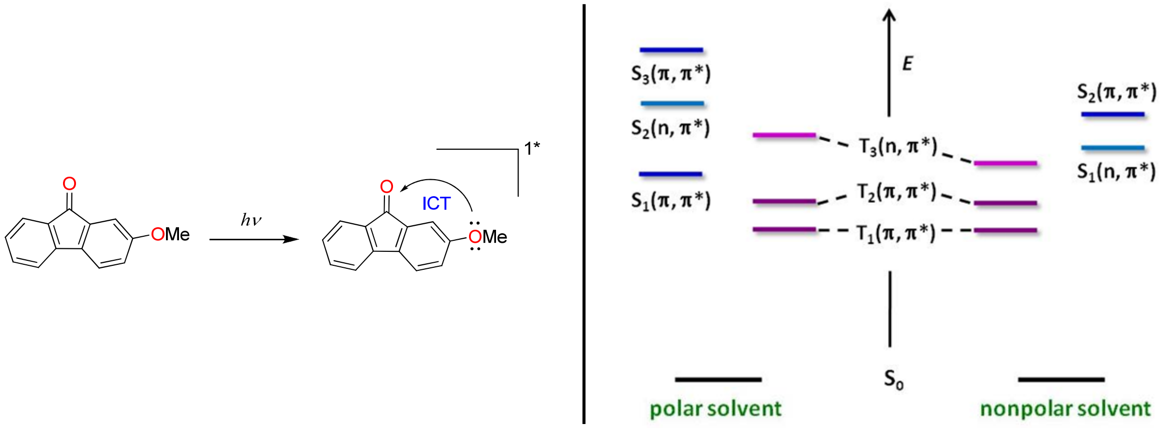


Fig. 4 Partial charge transfer in the excited state of meta-methoxyfluorenone **2** (left) and typical energetic ordering of the excited states of fluorenones in polar and nonpolar solvents (right).[29]

fluorescence emission becomes difficult to be detected for fluorenones **6-9**. With the data on quantum yields of fluorescence and rate of radiative decay (k_r) as derived from the fluorescence lifetimes, one may calculate the nonradiative rate constant (k_{nr}) for each fluorenone that includes the contribution of deactivation of S_1 state via isc. The rate constants thus derived for all fluorenones **1-9** are given in Table 1. We shall not consider the data in cyclohexane, where isc becomes competitive to deactivation via fluorescence from S_1 for some fluorenones such that the quantum yields of fluorescence and the rates of radiative decay for all ketones cannot be uniformly compared. Further, for some fluorenones, e.g., 2-methoxyfluorenone, the singlet excited state is of π,π* character in a nonpolar solvent such as methylcyclohexane.[3] In a polar solvent such as acetonitrile, the T_3 state should be pushed up in energy for all fluorenones to preclude any meaningful contribution by isc to the deactivation of S_1. Thus, the only mechanisms that depopulate the singlet-excited states turn out to be radiative and nonradiative decays. The fact that the nonradiative decay becomes promoted with increasing stabilization of the S_1 state is evident from the ca. 20–30-fold increase in k_{nr} for the multiply methoxy–substituted fluorenones **6** and **8** relative to the parent fluorenone **1**. Indeed, one observes a respectable correlation between the rates of k_{nr} and the singlet excitation energies calculated from the fluorescence maxima of all fluorenones in acetonitrile as shown in Fig. 5.

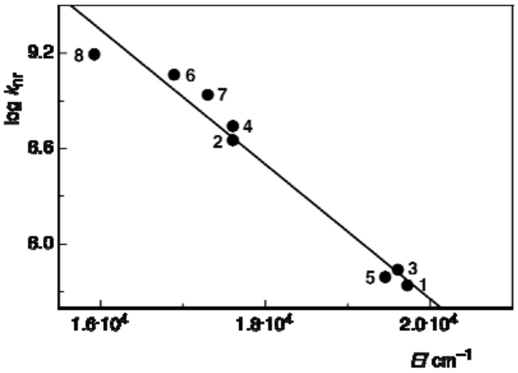


Fig. 5 Correlation between the nonradiative decay rate constants (log k_{nr}) with singlet excitation energies of fluorenones **1-8** in acetonitrile.

Alcohol quenching of singlet-excited states of fluorenones has been thoroughly established.[4,11] Given that hydrogen bonding is strengthened in the singlet-excited state, any factor that increases the charge on the carbonyl oxygen should enhance the hydrogen bond strength and hence the deactivation via hydrogen bonding. Indeed, for fluorenones with increasing number of methoxy groups, the fluorescence becomes undetectable attesting to the fact that quenching takes over radiative decay.

A comprehensive investigation of fluorenones substituted with methoxy groups at different positions thus reveals the importance of the location of substituents on the fluorenone core in promoting fluorescence or radiationless deactivation by way of modifying the energies of the singlet-excited states and their character. The knowledge uncovered herein is important, as for example, in the context of applications of polyfluorenes as emissive materials in OLEDs. It has been found that oxidation of polyfluorenes leads to generation of fluorenone impurities that contaminate the pure-blue emission.[16] Polyfluorenes substituted with methoxy groups at the meta positions may obviate the debilitating problem of contamination of blue emission by suppressing emission from oxidatively produced fluorenones. Further, in photoinduced electron-transfer dynamics studies, charge recombination and charge separation have been found to be strongly coupled to vibrational modes that are affected by hydrogen bonds.[17] Given that hydrogen bond strengths in the excited states can be modulated via methoxy substituents as revealed by k_{nr} rates, substituted fluorenones should serve as ideal substrates to gain more insights into photoinduced electron-transfer dynamics.

2.4 Effect of cucurbit[7]uril (CB7) encapsulation on the excited-state properties of fluorenones

Cucurbit[*n*]urils are a novel class of macrocyclic host molecules,[18-22] which have been widely employed for different applications. Recent examples of the latter include drug delivery,[30-32] protection and fluorescence enhancement of the fluorescent dyes,[33-35] development of fluorescent host–guest reporter pairs to monitor enzymatic reactions,[36] catalysis,[37,38] and for mimicking biological interactions in supramolecular assemblies.[39] Among different homologues, the heptameric CB7 has been found to exhibit relatively higher solubility in water and possess interior cavity dimensions suitable for encapsulation of small aromatic compounds. Due to its rigid structure, hydrophobic cavity and hydrophilic carbonylated portals on both sides, CB7 has been shown to provide a unique compartmentalized microenvironment to the included guest molecules. We, thus, wished to investigate how encapsulation of fluorenone and its derivatives in CB7 modifies their photophysical properties. In the present investigation, we have confined our studies to the parent fluorenone **1**. The limited solubility of substituted fluorenones in water and that of CB7 in a mixed organic–aqueous solvent system precluded more comprehensive investigations encompassing the influence of CB7 on the photophysical properties of the methoxy-fluorenones **2-9** in Fig. 1.

To examine the effect of CB7 on the photophysical properties of **1**, a 10 % (*v/v*) methanol–water mixture was chosen as the medium to ensure sufficient solubility of the host CB7 as well as the guest fluorenone **1**. An incremental addition of CB7 to the solution of **1** (8.2×10^{-5} M) led to progressive changes in the absorption spectra as shown in Fig. 6.

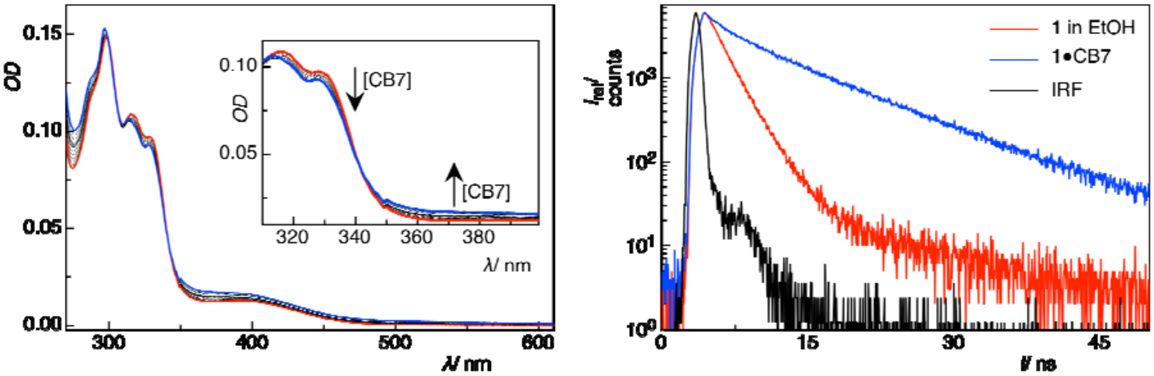


Fig. 6 Changes in the absorption of parent fluorenone **1** with incremental addition of CB7 (left, spectra were corrected for absorption by the CB7 sample); the optical densities for the spectral region between 310-400 nm are magnified in the inset. The fluorescence lifetime decay profiles of **1** in ethanol and in the presence of CB7 in 10% MeOH–H_2O (right). Note that the fluorescence measurements were performed with 82 μM solution of **1** in the absence and in the presence CB7; concentration of the latter was ca. 1.2 mM.

A careful inspection of changes in the absorption in the region between 310–500 nm reveals a hyperchromic change around 380 nm with a concomitant hypochromic shift at ca. 330 nm. Once the spectra were corrected for the intrinsic absorption of CB7 (which appeared to be more pronounced in the mixed organic-aqueous solvent than in neat water), one observes a clear isosbestic point at 343 nm. The observed spectral changes are attributed, in general, to the complexation-induced modification of the optical properties of encapsulated guests. However, the small changes observed in the optical densities of **1** with increasing concentration of CB7 precluded an accurate determination of the stability constant of the **1**•CB7 complex. This is due to the fact that the changes in the ground-state properties of **1** are not greatly influenced by environmental factors, as reflected from very subtle changes observed in the absorption properties of **1** with variation of solvents, cf. Table 1. Additionally, the limited solubility range of host and guest precluded optimization of the conditions for a full titration to be carried out. Indeed, such a complexation behavior of **1** and difficulty in determining the binding constants have also been noted previously with another host molecule, namely α-cyclodextrin.[40] To further establish the binding of **1** with CB7 and to gain insights concerning the structure of the **1**•CB7 complex, ^{1}H NMR spectroscopic measurements were performed. As shown in Fig. 7, the signals of all aromatic protons of fluorenone **1** are found to undergo upfield shift by up to 0.15 ppm in the presence of CB7. Based on the isosbestic point observed in the UV-vis absorption spectra and the shifts observed in the ^{1}H NMR signals of fluorenone **1** in the presence of CB7, we confirm that the stoichiometry of fluorenone **1** and CB7 complex is 1:1 in accordance with the CB7 complexes of various aliphatic and aromatic ketones investigated by Macartney and co-workers.[41] In general, protons of the aromatic guests located deep inside of CB7 cavities have been found to undergo upfield shift by ca. 0.8-1.00 ppm in NMR, while smaller upfield shifts have been noted for those lying closer to the portals of CB7.[42] Thus, shifts in the ^{1}H NMR signals of **1** in the presence of CB7 suggest that the aromatic moieties of the symmetrical fluorenone **1** are likely to be directed only marginally inward of the CB7 cavities. Thus, the carbonyl group of fluorenone **1** is likely to be positioned at the portals of CB7 experiencing a polar aprotic environment conferred by the carbonyl groups of CB7. The simple ^{1}H NMR pattern observed for the **1**•CB7 complex can be best reconciled from fast shuttling of the guest in-and-out of the complex.

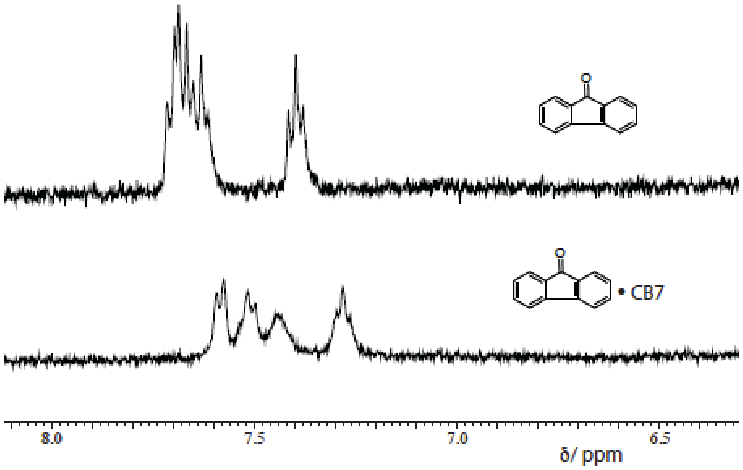


Fig. 7 ^{1}H NMR spectra of **1** in the absence and presence of CB7 in 10% (*v*/*v*) MeOH–d_4/D_2O.

Whereas the fluorescence emission of **1** in the medium employed was found to be too poor to allow spectral acquisition due to accelerated deactivation of the excited-state of **1** via hydrogen bond formation described above,[40] the effect of CB7 on the excited state properties of **1** was found to be quite significant. The complexation with CB7 was found to enhance the fluorescence as observed from the lifetime determinations, Fig. 6. The fluorescence decay in the presence of CB7 was best fitted to a biexponential function affording the following properties for the long- and short-lived components, respectively:[23] τ_1 = 9.39 ns, α_1 = 0.37; τ_2 = 2.86, α_2 = 0.63. The average fluorescence lifetime of **1** complexed with CB7 was calculated to be 5.3 ns with an error of ± 5%. It should be noted that the fluorescence quantum yield of **1** in 10% (*v*/*v*) MeOH–H_2O should be expected to be lower than that in EtOH based on the fact that the hydrogen bonding ability of H_2O is much better than that of EtOH. Evidently, the complexation-induced enhancement of the fluorescence lifetime should be traceable to the protection provided by CB7 to fluorenone **1** from hydrogen bonding interactions with the solvent. The fluorescence lifetime of 5.3 ns for **1**•CB7 in MeOH–H_2O, which is much higher than that in EtOH, suggests that fluorenone **1** experiences more polar aprotic environment that is akin to acetonitrile. We believe that the carbonyl group of fluorenone cannot penetrate into the cavity due to repulsions with the carbonyl groups at CB7 portals. Thus, the fluorenone carbonyl group is likely to be located at the portals of CB7 based on ^{1}H NMR spectral shifts. Otherwise, the results amply suggest that CB7 complexation permits photophysical properties to be examined in an aqueous medium for water-insoluble guests such as fluorenone **1**. The excited-state behavior of **1** complexed with CB7, as revealed by the fluorescence lifetime data, demonstrates the fact that fluorenone may serve as a probe of a polar microenvironment in which the hydrogen bonding interactions are weakened by spatial protection.

3 Experimental section

3.1 General aspects

All spectroscopic measurements were performed in spectroscopic grade solvents obtained from Sigma-Aldrich, Germany. The parent fluorenone **1** and 2-hydroxyfluorenone were purchased from Aldrich. UV–Vis measurements were carried out on a Shimadzu UV-1800 double-beam spectrophotometer which is accurate to ± 1 nm. Steady-state fluorescence measurements were performed on a FluoroMax$^{®}$-4: FM4-3000 spectrofluorometer (Horiba Jobin Yvon Technology) with an accuracy of ± 1 nm. The slit widths for both excitation as well as emission were fixed at 2.00 nm. The fluorescence spectra were corrected by subtracting the background scattering obtained for the respective solvent. Time-resolved fluorescence spectroscopy was conducted by time-correlated single photon counting (FLS920, Edinburgh Instruments) under air with a PicoQuant picosecondpulsed diode laser (λ_{ex}= 373 nm *ca*. 0.5 ns FWHM) for excitation. The instrument response function was measured by using a scatterer and the decays were fitted by using a reconvolution software supplied with the instrument.

3.2 Synthesis of fluorenone derivatives 2-9 and cucurbit[7]uril

While the parent fluorenone **1** was used as received, 2-hydroxyfluorenone was methylated with MeI in K_2CO_3/acetone to afford 2-methoxyfluorenone. All other methoxy-fluorenones were available from our previous investigation involving photochemical Pschorr cyclization of appropriately functionalized 2-bromobenzopheones.[43] CB7 was synthesized according to our previously reported method.[44]

3.3 UV-Visible and fluorescence spectroscopic investigation of fluorenone derivatives 1-9

Steady-state and time-resolved measurements of all fluorenone derivatives were performed in three different solvents that are nonpolar, polar aprotic and polar protic under air at ambient temperature (24 °C). All UV-visible absorption spectra were recorded for dilute solutions (ca. 5-8 × 10^{-5} M) to avoid complications arising from possible self-aggregation. Similar concentrations were employed for recording the emission spectra. The purity of the fluorenones was confirmed in each case by recording the excitation spectra with respect to three different emission wavelengths.

The fluorescence quantum yield of the parent fluorenone **1** in acetonitrile (Φ_f = 0.027) has previously been reported by Bohne and co-workers.[8] The same was independently re-determined, within error, for the commercially available fluorenone. Quantum yields of fluorescence of the parent fluorenone **1** in other solvents were corrected for the refractive index of the solvent. The quantum yields of all other fluorenones **2-9** were determined relative to fluorenone **1** in acetonitrile as a secondary standard. All photophysical parameters reported are based on at least two independent measurements.

4 Conclusions

The absorption and emission properties investigated for a broad set of methoxy–substituted fluorenones **1-9** show that the substituents at the meta positions with respect to the carbonyl group lead to a considerable red shift. While para substituents are found to affect neither the fluorescence quantum yields nor the lifetimes, those at the meta positions show significant variations. A cumulative effect is observed for the substituents in that the nonradiative decay (k_{nr}) becomes progressively dominant, at the expense of radiative relaxation (k_r), for fluorenones with increasing number of meta-methoxy substituents; e.g., the fluorescence quantum yields for fluorenones with three/four methoxy groups at the meta positions, i.e., **7-9**, become virtually insignificant. Accordingly, we find that the nonradiative decay (k_{nr}) can be increased by ca. 30 fold relative to the parent fluorenone **1** by trimethoxy substitution at the meta positions as in **8**. The predominance of nonradiative decay (k_{nr}) for meta-methoxy–substituted fluorenones is reconciled from stabilization of the singlet-excited state via partial charge transfer from the methoxy substituents to the carbonyl group. Indeed, a nice correlation is observed for the nonradiative (k_{nr}) rate constants, calculated based on quantum yields of fluorescence and fluorescence lifetime data, versus the singlet-excitation energies derived from fluorescence emission maxima of all fluorenones in a polar aprotic solvent such as acetonitrile. The excited-state properties are found to be influenced remarkably upon encapsulation in a macrocyclic host, namely CB7. The latter is found to not only enhance the fluorescence of the parent fluorenone **1** significantly, but to also increase the singlet lifetime considerably. The observed lifetime and changes in the absorption spectra suggest that fluorenone **1** is partly protected in the complex with CB7 from strong hydrogen bonding interactions and, thus, experiences a polar environment akin to that in acetonitrile; based on ^{1}H NMR analysis of **1** in the presence of CB7, a 1:1 host–guest complex formation has been confirmed. The results suggest that the hydrophobic fluorenone **1** can be employed as a probe to report on a polar microenvironment shielded from hydrogen bonding interactions in a polar protic solvent.

Acknowledgements

JNM is thankful to DST, India for generous funding and Alexander von Humboldt Foundation, Germany for a re-invitation, which facilitated the collaborative effort. IG and WMN would like to thank Deutsche Forschungsgemeinschaft (DFG, NA 686/5 and NA 686/6) for financial support. AM is thankful to CSIR (Council of Scientific and Industrial Research), India for a research fellowship.

References

1 T. Kobayashi and S. Nagakura, *Chem. Phys. Lett.*, 1976, **43**, 429-434.

2 L. Biczok and T. Berces, *J. Phys. Chem.*, 1988, **92**, 3842-3845.

3 L. Biczok, T. Berces and F. Marta, *J. Phys. Chem.*, 1993, **97**, 8895-8899.

4 L. Biczok, T. Berces and H. Linschitz, *J. Am. Chem. Soc.*, 1997, **119**, 11071-11077.

5 V. Samant, A. K. Singh, G. Ramakrishna, H. N. Ghosh, T. K. Ghanty and D. K. Palit, *J. Phys. Chem. A*, 2005, **109**, 8693-8704.

6 S. Hirai, M. Banno, K. Ohta, D. K. Palit and K. Tominaga, *Chem. Phys. Lett.*, 2007, **450**, 44-48.

7 G. J. Zhao and K. L. Han, *J. Phys. Chem. A*, 2007, **111**, 9218-9223.

8 R. S. Murphy, C. P. Moorlag, W. H. Green and C. Bohne, *J. Photochem. Photobiol., A*, 1997, **110**, 123-129.

9 M. K. Nayak and S. K. Dogra, *J. Photochem. Photobiol., A*, 2005, **169**, 299-307.

10 T. Yatsuhashi, Y. Nakajima, T. Shimada and H. Inoue, *J. Phys. Chem. A*, 1998, **102**, 3018-3024.

11 L. Biczok, T. Berces and H. Inoue, *J. Phys. Chem. A*, 1999, **103**, 3837-3842.

12 M. Jozefowicz, J. R. Heldt and J. Heldt, *Chem. Phys.*, 2006, **323**, 617-621.

13 L. Biczok, T. Berces, T. Yatsuhashi, H. Tachibana and H. Inoue, *Phys. Chem. Chem. Phys.*, 2001, **3**, 980-985.

14 L. A. Estrada, J. E. Yarnell and D. C. Neckers, *J. Phys. Chem. A*, 2011, **115**, 6366-6375.

15 T. D. Thangadurai, C. J. Lee, S. H. Jeong, S. Yoon, Y. G. Seo and Y. I. Lee, *Microchem. J.*, 2013, **106**, 27-33.

16 X. O. Gong, P. K. Iyer, D. Moses, G. C. Bazan, A. J. Heeger and S. S. Xiao, *Adv. Funct. Mater.*, 2003, **13**, 325-330.

17 H. N. Ghosh, K. Adamczyk, S. Verma, J. Dreyer and E. T. J. Nibbering, *Chem. Eur. J.*, 2012, **18**, 4930-4937.

18 J. Lagona, P. Mukhopadhyay, S. Chakrabarti and L. Isaacs, *Angew. Chem. Int. Ed.*, 2005, **44**, 4844-4870.

19 W. M. Nau, M. Florea and K. I. Assaf, *Isr. J. Chem.*, 2011, **51**, 559-577.

20 E. Masson, X. X. Ling, R. Joseph, L. Kyeremeh-Mensah and X. Y. Lu, *RSC Adv.*, 2012, **2**, 1213-1247.

21 J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540-541.

22 A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094-8100.

23 The two-component decays have been noted earlier for amino–substituted fluorenones. The fast decaying component has been attributed to relaxation of the original fluorescence state to the relaxed excited state, see: ref. 10.

24 J. N. Moorthy, S. Samanta, A. L. Koner and W. M. Nau, *Pure Appl. Chem.*, 2011, **83**, 841-860.

25 P. J. Wagner and B.-S. Park, in *Organic Photochemistry*, ed. A. Pawda, Marcel Dekker, New York, 1991; Vol. 11.

26 J. N. Pitts, D. R. Burley, J. C. Mani and A. D. Broadbent, *J. Am. Chem. Soc.*, 1968, **90**, 5902-5903.

27 P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, 1968, **90**, 5898-5899.

28 P. J. Wagner, A. E. Kemppainen and H. N. Schott, *J. Am. Chem. Soc.*, 1973, **95**, 5604-5614.

29 L. J. Andrews, A. Deroulede and H. Linschitz, *J. Phys. Chem.*, 1978, **82**, 2304-2309.

30 I. Ghosh and W. M. Nau, *Adv. Drug Deliv. Rev.*, 2012, **64**, 764-783.

31 D. Ma, G. Hettiarachchi, D. Nguyen, B. Zhang, J. B. Wittenberg, P. Y. Zavalij, V. Briken and L. Isaacs, *Nat. Chem.*, 2012, **4**, 503-510.

32 D. H. Macartney, *Isr. J. Chem.*, 2011, **51**, 600-615.

33 F. Biedermann, E. Elmalem, I. Ghosh, W. M. Nau and O. A. Scherman, *Angew. Chem. Int. Ed.*, 2012, **51**, 7739-7743.

34 A. C. Bhasikuttan, J. Mohanty, W. M. Nau and H. Pal, *Angew. Chem. Int. Ed.*, 2007, **46**, 4120-4122.

35 M. A. Rankin and B. D. Wagner, *Supramol. Chem.*, 2004, **16**, 513-519.

36 R. N. Dsouza, A. Hennig and W. M. Nau, *Chem. Eur. J.*, 2012, **18**, 3444-3459.

37 C. Klock, R. N. Dsouza and W. M. Nau, *Org. Lett.*, 2009, **11**, 2595-2598.

38 T. C. Lee, E. Kalenius, A. I. Lazar, K. I. Assaf, N. Kuhnert, C. H. Grun, J. Janis, O. A. Scherman and W. M. Nau, *Nat. Chem.*, 2013, **5**, 376-382.

39 R. B. Wang, B. C. MacGillivray and D. H. Macartney, *Dalton Trans.*, 2009, 3584-3589.

40 R. S. Murphy, T. C. Barros, J. Barnes, B. Mayer, G. Marconi and C. Bohne, *J. Phys. Chem. A*, 1999, **103**, 137-146.

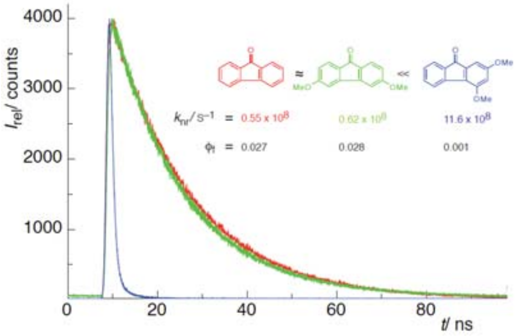
41 I. W. Wyman and D. H. Macartney, *Org. Biomol. Chem.*, 2008, **6**, 1796-1801.

42 A. L. Koner, I. Ghosh, N. Saleh and W. M. Nau, *Can. J. Chem.*, 2011, **89**, 139-147.

43 J. N. Moorthy and S. Samanta, *J. Org. Chem.*, 2007, **72**, 9786-9789.

44 C. Marquez, F. Huang and W. M. Nau, *IEEE Trans. Nanobiosci.*, 2004, **3**, 39-45.

Graphic for TOC



Fluorescence and radiationless deactivation of methoxy-substituted fluorenones are strongly guided by location(s) of the substituent(s) in the fluorenone core.

Keywords: Fluorenones, Excited State Properties, Fluorescence, Cucurbituril, Lifetimes