THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article

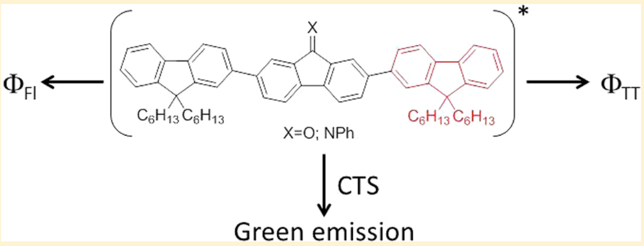
pubs.acs.org/JPCA

Oligofluorenes as Polymeric Model Compounds for Providing Insight into the Triplets of Ketone and Ketylimine Derivatives

Patricia Robert,† Andréanne Bolduc, and W. G. Skene*

Laboratoire de caractérisation photophysique des matériaux conjugués, Département de Chimie, Université de Montréal, CP 6128, Centre-ville, Montreal, QC

Supporting Information



ABSTRACT: A series of oligofluorenes ranging between one and three repeating units were prepared as structurally well-defined representative models of polyfluorenes. The photophysics of the oligofluorene models were investigated both by laser flash photolysis and steady-state fluorescence. The effects of the ketone and ketylimine functional groups in the 9-position on the photophysical properties, notably the triplet quantum yield (Φ_{TT}) by intersystem crossing and the absolute fluorescence quantum yields (Φ_{fl}), were investigated. The singlet depletion method was used to determine both the Φ_{TT} and molar absorption coefficients of the observed triplets (ε_{TT}). Meanwhile, the absolute Φ_{fl} were determined using an integrating sphere. It was found that both the ketone and ketylimine substituents and the degree of oligomerization contributed to quenching the oligofluorene fluorescence. For example, the Φ_{fl} was quenched 5-fold with the ketylimine and ketone substituents for the bifluorenyl derivatives compared to their corresponding 9,9-dihexyl bifluorenyl counterparts. Meanwhile, the Φ_{fl} quenching increased 14 times with the trifluorenyl ketone and ketylimine derivatives. Measured Φ_{TT} values ranged between 22 and 43% for the difluorenyl derivatives with ε_{TT} on the order of 13 000 $cm^{-1}\ M^{-1}$. The Φ_{TT} decreased to <10% concomitant with doubling of the ε_{TT} when the degree of oligomerization was increased to 3. A new fluorescence emission at 545 nm formed at low temperatures for the ketone and ketylimine oligofluorene derivatives. The emission intensity was dependent on the temperature, and it disappeared at room temperature.

INTRODUCTION

Fluorescent polymers have received much attention in part owing to their optical properties that are well suited for many uses, including sensors, lasers, and nonlinear optics.[1,2] The most important application of conjugated fluorescent polymers has been in terms of their use in organic light emitting diodes (OLEDs).[3−5] Of the many fluorescent polymers examined, fluorene (**1**) and its derivatives have attracted the most attention.[6−8] This is a result of their inherent high emission yields that are well suited for use in OLEDs, leading to devices with high performances.[9−14]

Despite their suitable photophysical properties for OLED usage, the fluorescence quantum yield (Φ_{fl}) and color emitted by polyfluorenes are highly contingent on both their substitution and their environment. This was evidenced via a series of structurally well-defined model compounds such as **7** and **8**.[15−17] The advantage of these models over their corresponding statistical copolymers is that uncertainties relating to chain-folding and randomness in the chain structure can be avoided, resulting in accurate structure−property studies.[18−21] These models successfully demonstrated that ketone defects in the 9-position of fluorene were in part responsible for both the decrease in fluorescence and undesired g-band green emission occurring at ca. 545 nm.[22−24] Studies with these representative polymeric models in addition to polyfluorene derivatives were additionally undertaken in attempts to assign the origins of the green emission.[25−27]

Although ketone defects, such as **2**, within polyfluorenes are undesired because they compromise the device efficiency and they contaminate the emission, the ketone function is nonetheless interesting. This is in part because functionality can be introduced into the conjugated network courtesy of the heteroatomic site.[28−32] For example, ketylimine formation is possible by condensation with amines.[33] The judicious choice of the amine used in ketylimine formation provides the means to adjust the polyfluorene properties such as solubility, electronic effects, color, and emission yields. Given that oligomeric fluorenes are generally accepted as suitable representative models for investigating the optoelectronic properties of their polymeric counterparts,[34−36] the photophysics of **4−9** (Figure 1) were subsequently investigated. These compounds were targeted because the effect of the ketylimine on the photophysics of the oligofluorenes could be examined. More importantly, the transient absorbance spectra and the quantum yield of triplet formation (Φ_{TT}) of these model compounds could additionally be investigated and compared to their corresponding fluorenone precursors and

Received: August 6, 2012
Revised: August 29, 2012
Published: August 29, 2012

dx.doi.org/10.1021/jp307781n | J. Phys. Chem. A 2012, 116, 9305−9314

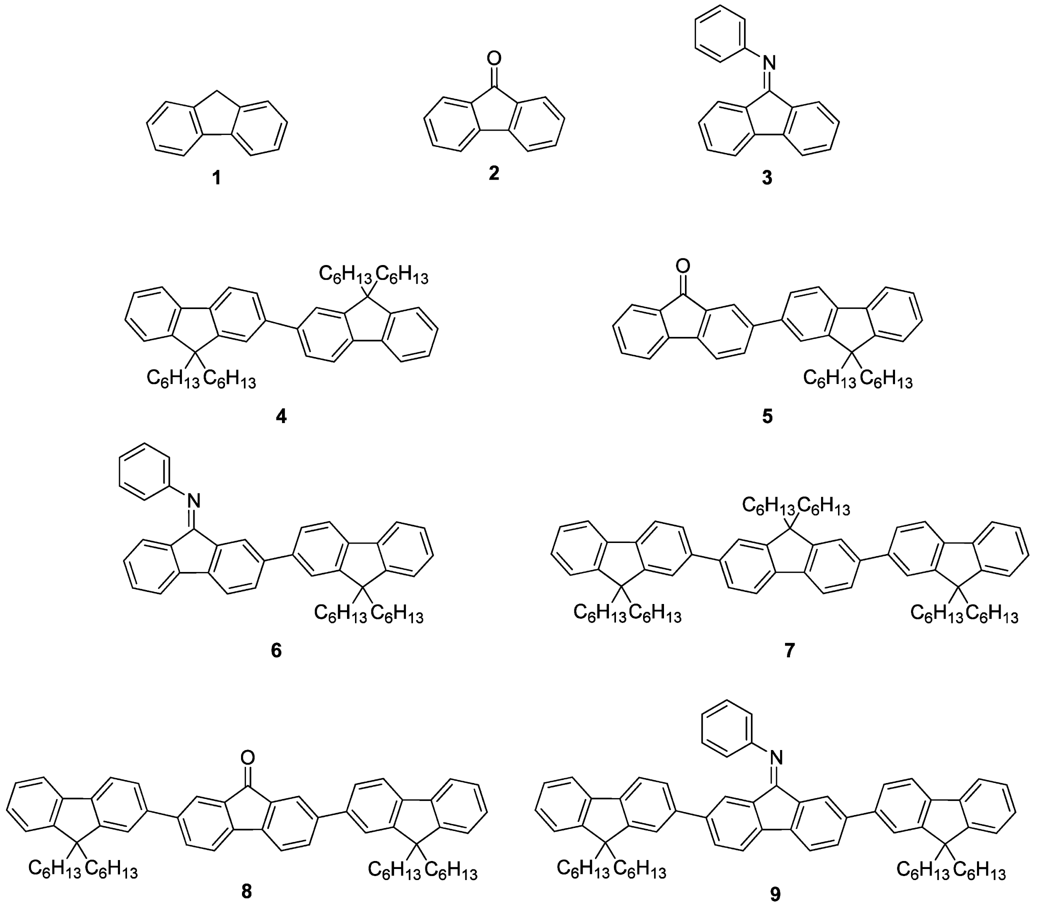


Figure 1. Series of oligofluorenes examined for triplet manifold studies.

9,9′-dialkylated oligofluorene counterparts. This is of importance given that the intrinsic singlet excited state deactivation of these compounds by intersystem crossing has not been previously investigated. The knowledge gained from investigating this often overlooked inherent fluorescence quenching mode is valuable for further deciphering the complex fluorescent deactivation mechanisms of polyfluorenes. Transient absorbance methods further provide vital information for assigning intra- vs intermolecular deactivation modes and for detecting short-lived intermediates. These are particularly significant, since the exact quenching modes of polyfluorene derivatives remain contentious.[37−39] The absolute fluorescence quantum yields (Φ_{fl}) of the oligofluorenes **4**−**9** were also investigated to further provide information about the deactivation modes, especially since these compounds have not been previously investigated using such absolute measurements.

■ EXPERIMENTAL SECTION

Materials and General Methods. All reagents were commercially available, and they were used as received unless otherwise stated. Anhydrous and deaerated solvents were obtained with an aluminum solvent purification system by Glass Contour. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer with the appropriate deuterated solvents.

Spectroscopic Measurements. Absorbance measurements were done on a Cary 500 spectrophotometer, and fluorescence measurements were performed on an Edinburgh Instruments FLSP-920 fluorimeter after deaerating the solvent for 20 min. Absolute quantum yields were measured using a commercial integrating sphere system. Lifetime measurements were done by the time correlated single photon counting method using a ps-pulsed laser at 375 nm.

Cryofluorescence. Cryofluorescence was performed using cryocuvettes from NSG Precision Glass and an Optistat cryostat from Oxford Instruments. The measurements were done in an anhydrous and deaerated mixture of 4:1 ethanol:methanol at given temperatures after the temperature had stabilized for 20 min. The change in solvent refractive index with temperature was taken into account for the emission measurements at various temperatures, according to eq 1.

$$\Phi_{x\mathrm{K}} = \Phi_{300\mathrm{K}} \cdot \left(\frac{\eta_{x\mathrm{K}}}{\eta_{300\mathrm{K}}}\right)^2 \qquad (1)$$

Transient Absorbance Spectroscopy. Laser flash photolysis analyses were done using a mini-laser flash photolysis (Luzchem) system excited at 355 nm with the third harmonic of a Nd:YAG laser. The solutions were prepared with an absorbance between 0.3 and 0.4 at 355 nm. The solutions were prepared in either dichloromethane or a 1:1 mixture of dichloromethane/methanol, depending on the solubility of both the compounds and quencher. The transient absorbance spectra were generated by averaging the transient kinetics over 5−7 shots per wavelength that were recorded at different intervals after the laser pulse. Quenching kinetics were done by measuring the change in the transient absorbance spectra as a function of quencher. Quenchers used for assigning the observed transients were 1,3-cyclohexadiene, 2-methylnaphthalene, β-carotene, and methylviologen.

The quantum yields of intersystem crossing (Φ_{ISC}), which are equal to the quantum yields of triplet formation (Φ_{TT}), were determined by relative actinometry via the singlet depletion method.[40−42] The molar absorption coefficients of both the singlet (ε_s) and triplet (ε_{TT}) of **3**−**9** are required for the singlet depletion method. Values of ε_s were measured by preparing stock solutions of **3**−**9** of precise concentrations. The solutions were sequentially diluted and the absorbance measured, with the desired ε_s derived from the slope of absorbance as a function of concentration. The wavelength for the singlet studies was selected such that it did not overlap with the transient produced in the transient absorbance spectroscopy measurements. The ε_{TT} value of the compounds was determined, as per eq 2, with ΔAbs referring to the maximum signal intensity measured at the corresponding absorbance maximum. The kinetics of both the ground-state bleaching and triplet were measured on short-time scales for obtaining a maximum number of data points at the maximum signal intensity. The signal maximum of both the ground state and triplet were measured as a function of laser power, as per Figure 4A. The laser Q's switch delay was adjusted to vary the laser power output. The desired ε_{TT} was calculated from the ratio of the two slopes, with the triplet and singlet signals being a function of laser power.

$$\varepsilon_{TT} = \varepsilon_s \frac{\Delta \mathrm{Abs}_{TT}}{\Delta \mathrm{Abs}_s} \qquad (2)$$

Benzophenone ($\Phi_{TT} = 1$; $\varepsilon_{TT} = 7200\ \mathrm{M^{-1}\ cm^{-1}}$) was taken as the reference to determine the Φ_{TT} values of **3**−**9** with the benzophenone data being taken from literature values measured in acetonitrile.[43−45] Optically matched samples at 355 nm of benzophenone and the given compounds were prepared in anhydrous and deaerated dichloromethane. The transient kinetics were measured at the corresponding triplet absorbance maxima as a function of laser power. The Φ_{TT} was calculated according to eq 3 (see ref 46), where ΔAbs is the maximum signal corresponding to the triplet (λ_2) that was measured at the maximum for the corresponding transients. This signal was measured as a function of laser power, as seen in Figure 4B.

$$\Phi_{TT}^{\mathrm{Sample}} = \frac{\varepsilon_{TT}^{\mathrm{Reference}}(\lambda_1)}{\varepsilon_{TT}^{\mathrm{Sample}}(\lambda_2)} \frac{\Delta \mathrm{Abs}^{\mathrm{Sample}}(\lambda_2)}{\Delta \mathrm{Abs}^{\mathrm{Reference}}(\lambda_1)} \cdot \Phi_{TT}^{\mathrm{Reference}} \qquad (3)$$

Synthesis. The synthesis of **3**, **5**, **6**, **8**, and **9** was done according to known means.[33,47]

2-Bromo-9,9-dihexyl-9H-fluorene.[48] 2-Bromofluorene (1.6 g, 6.54 mmol) was dissolved in DMSO (35 mL). 1-Bromohexane (2.2 mL, 15.59 mmol), benzyltriethylammonium chloride (75 mg, 0.33 mmol), and a solution (14 mL) of sodium hydroxide (7.79 g, 0.19 mol) were added to the mixture. The color of the mixture subsequently changed from orange to violet, and the mixture was stirred under nitrogen for 21 h. The reaction mixture was then poured into water (80 mL). The crude product was extracted with ethyl acetate (4 × 50 mL), and the organic layer was washed with water (4 × 100 mL). It then was dried with $MgSO_4$, filtered, and concentrated in vacuo. The title compound was isolated as a colorless oil (2.24 g, 5.38 mmol, 82%) after purification by silica gel flash chromatography using hexanes (100%). ^{1}H NMR (acetone-d_6): δ = 7.81−7.79 (m, 1H), 7.74 (d, J = 8 Hz, 1H), 7.64 (d, J = 2 Hz, 1H), 7.47 (dd, J = 8.2 Hz, 1H), 7.47−7.45 (m, 1H), 7.37−7.32 (m, 2H), 2.09 (s, 2H), 1.13−0.99 (m, 12H), 0.76 (t, J = 4.7 Hz, 6H), 0.60−0.56 (m, 4H).

(9,9-Dihexyl-9H-fluoren-2-yl)boronic Acid.[49] To 2-bromo-9,9-dihexyl-9*H*-fluorene (1.53 g, 3.67 mmol) dissolved in anhydrous THF (23 mL) was added *n*-BuLi (2.2 M in hexanes, 2 mL) at −78 °C. The reaction mixture turned orange, and it was allowed to react for 1 h before triethylborane (1 mL, 6.9 mmol) was added dropwise. After stirring for 14 h, water (23 mL) was added to the reaction mixture and it was allowed to further stir for 1 h. 2 M HCl (18 mL) solution was added, and the THF was evaporated under vacuo. The crude product was extracted with ethyl acetate (4 × 70 mL), and the organic layer was dried with $MgSO_4$, filtered, and then concentrated under vacuo. The product was purified by flash chromatography using dichloromethane (100%) to afford the title compound as a white powder, which was used immediately without additional characterization.

*9,9,9′,9′-Tetrahexyl-9H,9′H-2,2′-bifluorene (**4**).*[50] To 2-bromo-9,9-dihexyl-9*H*-fluorene (2.20 g, 5.30 mmol), (9,9-dihexyl-9*H*-fluoren-2-yl)boronic acid (4 g, 10.6 mmol) dissolved in toluene (8 mL) was added a solution (10 mL) of sodium carbonate (28 mg, 0.18 mmol). The mixture was refluxed for 1 h under nitrogen, and then, palladium tetrakis(triphenylphosphine) (35.5 mg, 0.02 mmol) was added and the mixture was protected from light. After 2 days, the reaction mixture was poured into hexanes (125 mL). The product was extracted with a saturated solution of sodium chloride (3 × 50 mL). The organic layer was dried with $MgSO_4$, filtered, and then concentrated under vacuo. The crude product was purified by silica gel flash chromatography using hexanes (100%) to give the product as a white powder (4.5 mg, 0.13%). ^{1}H NMR (acetone-d_6): δ = 7.77 (d, J = 8 Hz, 2H), 7.67 (d, J = 2 Hz, 2H), 7.54 (dd, J = 2, 8 Hz, 2H), 2.12−2.07 (m, 4H), 1.14−1.01 (m, 12H), 0.77 (t, J = 7, 14 Hz, 6H), 0.64−0.56 (m, 4H). ^{13}C NMR (chloroform-d): δ = 151.4, 150.9, 140.8, 140.5, 140.3, 126.9, 126.8, 126.0, 122.9, 121.4, 119.8, 119.7, 55.2, 40.4, 31.5, 29.7, 23.8, 22.5, 13.9.

2,7-Dibromo-9,9-dihexyl-9H-fluorene.[51] 2,7-Dibromofluorene (0.41 g, 1.27 mmol) was dissolved in DMSO (15 mL), and phenyltriethylammonium chloride (188 mg, 0.82 mmol) was added. The mixture was heated at 75 °C. After 1 h, 1-bromohexane (1 mL, 7.25 mmol) and a sodium hydroxide (1.74 g, 15 mL) solution were added. After 17 h, the reaction mixture was poured into 1.44 M HCl (100 mL). The crude product was extracted with ethyl acetate (50 mL) and water (4 × 150 mL). The organic layer was further washed with a saturated solution of sodium chloride (3 × 50 mL) and the organic layer was then extracted, dried with $MgSO_4$, filtered, and concentrated under vacuo. The crude product was purified by silica gel flash chromatography using hexanes (100%) to give the product as a white powder (0.81 mmol, 64%). ^{1}H NMR (acetone-d_6): δ = 7.92−7.84 (m, 6H), 7.77 (dd, J = 2, 8 Hz, 2H), 7.56−7.48 (m, 2H), 7.38−7.35 (m, 4H), 2.10 (s, 8H), 1.12−1.11 (m, 24H), 0.89−0.88 (m, 12H), 0.77 (t, J = 14, 7 Hz, 8H). ^{13}C NMR (acetone-d_6): δ = 153.2, 139.8, 130.7, 126.6, 122.1, 121.7, 56.3, 40.0, 29.8, 29.7, 29.6, 29.4, 29.2, 29.0, 24.0, 22.7.

*9,9,9′,9′,9″,9″-Hexahexyl-9H,9′H,9″H-2,2′:7′,2″-terfluorene (**7**).*[52] In toluene (2.5 mL) were dissolved 2,7-dibromo-9,9-dihexyl-9*H*-fluorene (377 mg, 0.54 mmol), (9,9-dihexyl-9*H*-fluoren-2-yl)boronic acid (178 mg, 0.47 mmol), and sodium carbonate (10.3 mg, 0.11 mmol). The reaction mixture was refluxed for 1 h under nitrogen while it was protected from light. Palladium tetrakis(triphenylphosphine) (14 mg, 0.014 mmol) was then added. The reaction mixture was poured into hexanes (80 mL) after refluxing under nitrogen for 48 h. The crude product was extracted with a saturated solution of sodium chloride (3 × 75 mL), and the organic layer was dried with $MgSO_4$, filtered, and then concentrated under vacuo. The crude product was purified by silica gel flash chromatography using hexanes and ethyl acetate (99:1). The product was isolated as a colorless viscous oil (324 mg, 86%). ^1H NMR (chloroform-*d*): δ = 7.88−7.86 (m, 4H), 7.79 (d, J = 7 Hz, 2H), 7.74−7.69 (m, 8H), 7.44−7.36 (m, 6H), 2.15−2.08 (m, 12H), 1.21−1.15 (m, 36H), 0.89−0.81 (m, 30H). ^{13}C NMR (chloroform-*d*): δ = 151.8, 151.5, 150.9, 140.8, 139.9, 126.9, 126.8, 126.1, 126.0, 122.9, 121.5, 121.4, 119.9, 119.9, 119.7, 55.3, 55.2, 40.4, 31.5, 29.7, 22.6, 22.5, 14.0.

■ RESULTS AND DISCUSSION

Transient Absorbance Spectroscopy. Transient absorbance spectroscopy of the compounds was investigated via laser flash photolysis. This was done to identify and quantify the transients produced upon photoexcitation. Given the potential complexity of assigning the transients for **4**−**9**, the transient absorbance spectrum of **2** was first investigated as a benchmark. This is of importance because the efficiency of fluorenone triplet formation via intersystem crossing is known to be dependent on solvent polarity.[53,54] In addition, there are limited characterization details of these transients in either dichloromethane or the 1:1 dichloromethane/methanol mixtures used for the current study.[41,43] Dichloromethane was the preferred solvent because of the high solubility of **4**−**9** in this polar aprotic solvent. It is also the solvent of choice for polymer studies. Therefore, the results can directly be compared to similarly reported systems. Meanwhile, the binary mixture was required for the mutual solubility of the quencher and the compounds studied and for cryofluorescence measurements.

The transient absorbance spectrum of **2** obtained in dichloromethane is shown in Figure 2A. It is evident that a transient strongly absorbs at approximately 440 nm concomitant with a weak absorbance at ca. 630 nm. These absorbances are consistent with the known triplet of **2**.[55] The triplet intermediate was in part assigned from the observed unimolecular decay (black line inset Figure 2A) in addition to the similar absorbances of triplet fluorenone measured in other solvents.[41,43] Absolute assignment of the transient was done by quenching the transient with 1,3-cyclohexadiene. Not only is this a known triplet quencher,[56,57] but it is invisible in the spectroscopic window used for the transient studies. This leads to clean transient absorbance spectra, and it makes for easy assignment of the transient. The resulting transient absorbance spectrum of **2** upon the addition of 0.03 mM 1,3-cyclohexadiene is seen in Figure 2A (red circles). The resulting spectrum is quenched with the addition of the diene. The quenching is confirmed by comparing the kinetic traces measured at 420 nm in both the absence and presence of the diene (red circles inset Figure 2A). Both the observed unimolecular decay kinetics and the absorbance quenching with 1,3-cyclohexadiene confirm that the transient of **2** produced upon excitation at 355 nm is the triplet, whose maximum absorbance is at 420 nm.

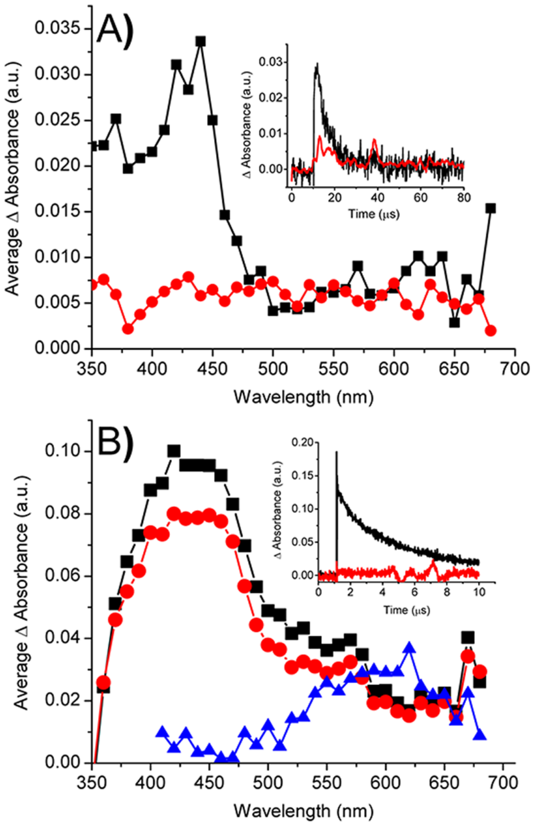


Figure 2. (A) Transient absorbance spectra of **2** measured in dichloromethane at 1.04 μs after the laser pulse in the absence (black ■) and with the addition of (red ●) 1,3-cyclohexadiene. Inset: kinetic trace monitored at 420 nm in the absence (black line) and with the addition (red line) of 1,3-cyclohexadiene. (B) Transient absorbance spectra of **5** measured in a 1:1 dichloromethane/methanol mixture excited at 355 nm and measured 28.2 (black ■) and 39.5 μs (red ●) after the laser pulse in the absence and with the addition of 1,3-cyclohexadiene (blue ▲) measured 1.6 μs after the laser pulse. Inset: kinetic decay traces of **5** measured in the absence (black line) and presence of 1,3-cyclohexadiene (red line) monitored at 450 nm after excitation at 355 nm.

The transient absorbance spectra of the ketone and ketylimine oligomers were subsequently investigated in dichloromethane. Similar to **2**, **5**−**8** each exhibited a strong absorbance at ca. 440 nm and a weaker absorbance at approximately 620 nm. The observed first order kinetics suggest that the transient is the triplet. This was confirmed by quenching with 1,3-cyclohexadiene. As seen in both the inset and the transient absorbance spectrum of **5** (Figure 2B), the species is quenched with the addition of 1,3-cyclohexadiene. This was also the case for **6**−**9**. The transient was also examined in the addition of methylviologen, which is an oxidant and whose corresponding cation absorbs at 607 nm in acetonitrile.[58,59] Given the limited solubility of methylviologen in neat dichloromethane, a 1:1 dichloromethane/methanol mixture was used. A new absorbance at ca. 600 nm was observed in the transient absorbance spectrum (see the Supporting Information) for both **5** and **8**. The lifetime of the transient at 600 nm was greater than 10 μs, and it decayed with bimolecular kinetics. This suggests that the ketyl derivatives can be photo-oxidized, resulting in the radical cation.

Similar transient absorbance spectra features between **2** and the ketylimine derivative (**3**) were expected. However, no transient absorbance signal was observed with **3**. To some extent, this is not surprising, since the imine is known to rapidly deactivate excited states.[44,60−62] In contrast, a transient was observed at 420 and 450 nm, respectively, for **6** and **9**. Both transients decayed with first order kinetics, and these transients were also quenched with 1,3-cyclohexadiene.

The transients **4** and **7** were additionally examined to confirm that their triplet was produced. This is of particular interest, since the triplets of these derivatives have never been previously investigated. As seen in Figure 3, **4** produces a transient that is visible at 520 nm, while that of **7** absorbs at 480 nm (Supporting Information). The transient observed for both **4** and **7** was assigned to the triplet owing to the first order decay and its disappearance in the presence of 1,3-cyclohexadiene.

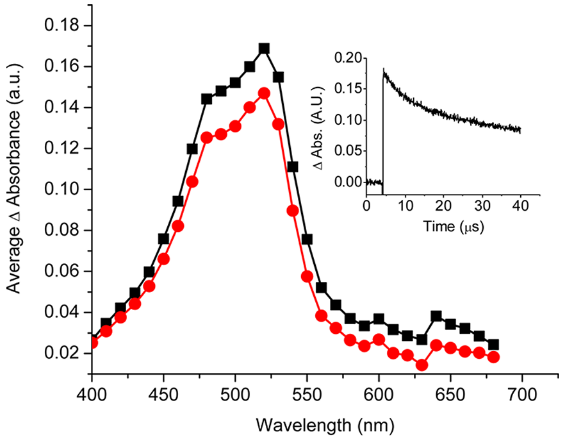


Figure 3. Transient absorbance spectra of **4** measured in dichloromethane 5.31 (black ■) and 8.16 μs (red ●) after the laser pulse at 355 nm. Inset: decay kinetics of **4** measured at 520 nm.

Triplet Quantum Yield Determination. The collective transient data of **5**, **6**, **8**, and **9** confirm that the triplet is produced upon irradiation. As seen in Table 1, the maximum absorbance of the triplet is somewhat dependent on the degree of oligomerization. It is further apparent from the collective data that the triplet of the ketone and ketylimine containing oligomers is bathochromically shifted from the all-fluorene derivatives. This is in part owing to their different degrees of conjugation. This notwithstanding, only qualitative results relating to the triplet state can be derived from the transients. Given that the singlet excited state is competitively deactivated by nonradiative intersystem crossing, quantifying the amount of fluorescence lost due to triplet formation is desired.

Triplet quantification is typically done by relative actinometry. This involves comparing the amount of the triplet signal for the given sample at its absorbance maximum ($\Delta\mathrm{Abs}(\lambda_2)$) relative to a standard with a known Φ_{TT}, which is measured at its triplet maximum ($\Delta\mathrm{Abs}(\lambda_1)$), according to eq 3. The desired triplet quantum yield can only be derived if the molar absorption coefficient ($\varepsilon_{\mathrm{TT}}(\lambda_2)$) of the sample's triplet is known at the given wavelength. This is problematic for **4**−**9**, given the limited previous triplet investigations of these compounds.

Knowledge of the $\varepsilon_{\mathrm{TT}}$ is not required from relative actinometry when the same triplet is produced for both the sample and the reference. In such a case, eq 3 can be simplified to eq 4, with ΔAbs being the signal observed for the transient as a function of excitation energy. This is the case for triplet quenchers such as naphthalene and β-carotene.[63] These deactivate the given triplets by energy transfer to provide their corresponding triplets that are visible at 420 and 515 nm, respectively.[42,43,64] Unfortunately, these and other standard triplet quenchers could not be used because of their overlapping triplets with those of **4**−**9**. This would lead to significant errors in deriving the desired Φ_{TT}. For this reason, the $\varepsilon_{\mathrm{TT}}$ of the oligofluorenes had to be determined from eq 2 and the desired Φ_{TT} had to then be calculated according to eq 3.

$$\Phi_{\mathrm{TT}}^{\mathrm{Sample}} = \frac{\Delta\mathrm{Abs}_{\mathrm{Sample}}(\lambda_1)}{\Delta\mathrm{Abs}_{\mathrm{Reference}}(\lambda_1)} \cdot \Phi_{\mathrm{TT}}^{\mathrm{Reference}} \qquad (4)$$

The $\varepsilon_{\mathrm{TT}}$ values of **4**−**9** were determined by the singlet depletion method, according to eq 2.[40] This method is applicable given that the respective ground and excited state absorbance spectra of the compounds do not overlap. The method further requires the absence of fluorescence in the transient absorbance spectra. The singlet depletion method further assumes that all the excited singlet states produced upon excitation are either returned to the ground state (vide infra) or form the triplet state. The ground state molar absorption coefficients (ε_{s}) of **4**−**9** were measured at their corresponding maximum. The required $\varepsilon_{\mathrm{TT}}$ (Table 1) were calculated from the ratio of the two slopes from Figure 4A. The slopes were derived

Table 1. Various Spectroscopic Properties of Fluorene Derivatives Measured in Dichloromethane

compound	ε_{s}[a] ($\mathrm{cm^{-1}\,M^{-1}}$)	$\varepsilon_{\mathrm{TT}}$[b] ($\mathrm{cm^{-1}\,M^{-1}}$)	λ_{fl} (nm)	λ_{TT}[c] (nm)	Φ_{TT}[d] (λ)	Φ_{fl}[e]	$\Phi_{\mathrm{fl(MeOH)}}$
1[f]	n/d[g]	40 000	302	376	0.03	0.70	n/d[g]
2	1600 (309)	5900[h]	505	430/650	0.94[h]	0.02	<0.02
3	8500 (300)	–	478	–	–	0	<0.02
4	22 000 (330)	14 000	380	520	0.22	0.53	0.77
5	38 000 (295)	13 000	560	410/610	0.36	0.11	<0.02
6	27 000 (295)	9000	559	410/650	0.43	0.06	0
7	70 000 (352)	79 000	395	480	0.09	0.71	0.98
8	31 000 (310)	26 000	584	440/580	0.08	0.04	0.07
9	17 000 (295)	30 000	566	440/520	0.02	0.02	<0.02

[a] Ground state molar absorption coefficients measured at the wavelength reported in parentheses. [b] Triplet molar absorption coefficient at λ_{TT} derived from the singlet depletion method. [c] Triplet absorbance maximum. [d] Yield of triplet formation determined from the singlet depletion method using benzophenone as a reference.[45] The values were calculated at λ_{TT}. [e] Absolute fluorescence quantum yield by using an integrating sphere with 2% being the lowest Φ_{fl} that can accurately be measured. [f] Literature values.[71,72] [g] Not determined. [h] Literature values.[73]

by monitoring the change in the ground state bleaching and the triplet formed as a function of laser power.

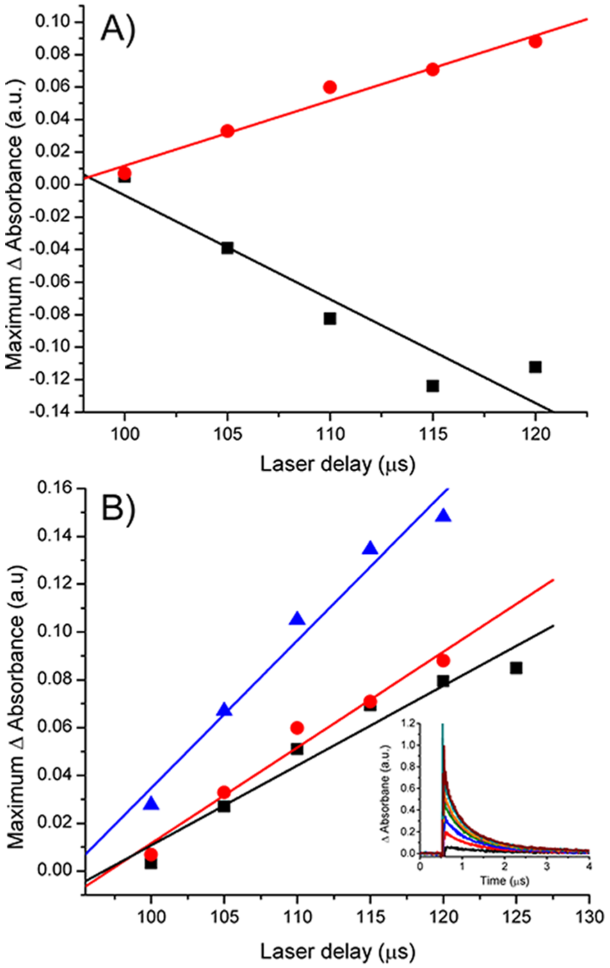


Figure 4. (A) The maximum ground state bleaching (black ■) and triplet (red ●) signals of **5** measured as a function of laser power at 295 and 410 nm, respectively. (B) Variation of the triplet intensity of benzophenone (blue ▲), **5** (black ■), and **6** (red ●) measured as a function of laser power at 525, 410, and 410 nm, respectively, of optically matched samples at 355 nm. Inset: variation of benzophenone triplet kinetics measured as a function of decreasing laser power measured at 450 nm.

The Φ_{TT} values of **4**−**9** were derived according to eq 3 using benzophenone as the reference (Φ_{TT} = 1; ε_{TT} = 7200 M^{-1} cm^{-1}).[43−45,65] For this, optically matched samples at 355 nm of benzophenone and the desired oligofluorene were prepared. The maximum signal of triplet benzophenone was measured at 525 nm as a function of laser power. Similarly, the triplets of **4**−**9** were measured at the corresponding triplet absorbance maximum. The desired Φ_{TT} was then derived from the ratio of the slopes of Figure 4B and by taking into account the ε_{TT} of the reference and that of the fluorene derivatives, derived from eq 2.

From the calculated Φ_{TT} in Table 1, it is evident that all the compounds produce their triplet in appreciable amounts. To validate the results calculated from the singlet depletion method, the triplet of **2** was also examined. This was chosen as a reference because its Φ_{ISC}, and hence Φ_{TT}, has extensively been examined.[54,66−70] While the Φ_{TT} of **2** has not previously been measured directly in dichloromethane using the singlet depletion method, the calculated value (Φ_{TT} = 0.94) from eqs 2 and 3 is nonetheless consistent with previously reported values that were measured via singlet oxygen in organic solvents of similar polarity. The consistent Φ_{TT} measured for **2** by the different methods validates the singlet depletion method as a viable means for deriving ε_{TT} of the oligofluorenes.

The effect of increasing the degree of conjugation on the Φ_{TT} for the oligofluorenes is evident when comparing **1**, **4**, and **7**. The triplet is reduced by ca. 10% with the addition of a fluorene to the structure. The same trend of triplet yield reduction with increasing degree of conjugation is further seen with the ketone derivatives **5** and **8**. In fact, Φ_{TT} is reduced by a third with the subsequent addition of the fluorene relative to the native **2**. The effect of the degree of conjugation on the triplet is further apparent from the ε_{TT}. The measured ε_{TT} values imply that the triplet of the triads absorb much stronger than their corresponding diads. The latter in turn absorb much stronger than their corresponding monomers. The measured Φ_{TT} values confirm that the triplet manifold is formed for all of the compounds, with the triplet diads being formed the most. In contrast, the triplet is formed in less than 10% for the triads. Therefore, while the triplet is formed, it is a minor deactivation pathway of the singlet excited state for the triads.

Fluorescence. The absolute fluorescence quantum yields (Φ_{fl}) of the fluorenes were additionally examined using an integrating sphere. This method is preferred over relative actinometry because a reference having similar absorbance, fluorescence, and quantum yield to the compound of study is not required. The Φ_{fl} values determined with an integrating sphere are absolute values with higher precision than values determined by relative actinometry. Measuring the absolute Φ_{fl} is of importance given that the fluorescence yield of the oligofluorenes has exclusively been measured by relative means. Absolute values are further desired for accurately understanding the deactivation modes of the oligofluorenes. Accurate values are of importance for indirectly determining the contribution of other deactivation modes according to the energy conservation law: $\Phi_{TT} + \Phi_{fl} + \Phi_{IC} + \Phi_{other\ modes} = 1$. The Φ_{fl} values of **2**−**9** were measured in dichloromethane to correlate the data with the triplet results.

The Φ_{fl} was dependent on the degree of oligomerization similar to what was seen with the Φ_{TT}. The Φ_{fl} are higher for the triads than the diads. As expected, **4** and **7** fluoresce more than their corresponding ketone and ketylimine derivatives. Also, the sum of Φ_{fl} and Φ_{TT} are nearly unity, confirming the absence of other deactivation processes. This was supported by measuring the Φ_{fl} at low temperatures in methanol. The absence of increased fluorescence at low temperatures further confirms that deactivation by internal conversion is not a viable deactivation mode.

In contrast to the all-fluorene derivatives, the combined respective Φ_{fl} and Φ_{TT} of **5**, **6**, **8**, and **9** are considerably less than unity. This confirms the presence of deactivation modes other than fluorescence and intersystem crossing. While fluorenone is known to readily undergo photoreduction to form a radical anion,[74,75] the presence of this intermediate can be precluded in part owing to the absence of a visible radical anion in the transient absorbance measurements. Moreover, the formation of radical ions would eventually lead to product degradation with prolonged irradiation. Such products were not observed.

The excited state deactivation modes of the ketone and ketylimine fluorene derivatives were further investigated using cryofluorescence. Deactivation processes, in particular those occurring by internal conversion (IC) such as rotation around the fluorene−fluorene bond, can be identified from such low temperature fluorescence measurements, according to $\Phi_{IC} = \Phi_{fl}$ (77 K) − Φ_{fl} (300 K).[56,57,76] Deactivation by internal conversion is suppressed at reduced temperatures, resulting in fluorescence enhancement. This is in contrast to singlet excited state deactivation by ISC to the triplet state that is an inherent process, which is temperature independent. While fluorescence and triplet measurements were done in dichloromethane, this was not a suitable solvent for low temperature measurements. This is because it does not form the required glass matrix at 77 K for accurate fluorescent measurements. Cryofluorescence measurements were therefore done in a 1:4 methanol/ethanol glass forming matrix. This solvent mixture was preferred over the commonly used EPA solvent mixture (diethylether/pentane/ethanol)[77] because it easily forms a glass matrix and it is easier to prepare.[78] The fluorescence at room temperature was also examined in this solvent in order to correlate the data with the low temperature measurements. The measurements were further done in this solvent to confirm that there is little solvent dependent fluorescence between the two polar solvents (dichloromethane and ethanol/methanol mixture). According to Table 1, the Φ_{fl} values of **4** and **7** increase slightly in the ethanol matrix compared to dichloromethane. In contrast, the Φ_{fl} of **5**, **6**, and **9** decreased only marginally in the methanol/ethanol mixture, when taking into account the uncertainties of the absolute measurements. The measured Φ_{fl} nonetheless confirm that the oligofluorene fluorescence is not quenched by hydrogen bonding in the protic solvent.

The Φ_{fl} were corrected for the temperature dependent solvent refractive index change using eq 1. This takes into account the change of the solvent refractive index at the given temperature relative to the absolute quantum yield measured at room temperature (Φ_{298K}).[78,79] Significant fluorescence enhancement would be seen in the 300−450 nm range if IC was a major mode of deactivation. As seen in Figure 5, there is little variation in the fluorescence spectra at reduced temperatures. In fact, the Φ_{77K}/Φ_{298K} ratio for **8** and **9** is unity. This confirms the absence of deactivation modes via IC (vide supra). In contrast, a new emission occurs between 500 and 650 nm. While the emission increase cannot be quantified, the trend of increasing emission with reduced temperature is evident from the inset of Figure 5. It should be noted that the low temperature emission centered at 545 nm is reversible and it disappears at room temperature. Moreover, the structured fluorescence at 400 nm did not vary with temperature or prolonged irradiation times. This confirms the absence of product photodegradation. While the emission at ca. 545 nm at low temperature was found exclusively for **2**, **5**, **6**, **8**, and **9**, it was more pronounced for the fluorenone derivatives. This indicates that the heteroatomic substitution at the 9-position contributes to the red-shifted emission.

While the fluorescence of **2** is known to be red-shifted upon progressing from nonpolar to polar solvents, this is not responsible for the observed temperature induced red-shifted emission observed in Figure 5.[80,81] Instead, the new emission at 545 nm is from a charge transfer state (CTS) between the electron accepting fluorenone/ketylimine moiety and electron donating fluorene.[82,83] This was previously confirmed by incorporating various amounts of fluorenone into polyfluorenes that resulted in significant increases from the low energy emission at 545 nm.[84−86] The identically shifted emissions of **5**, **6**, **8**, and **9**, taken together with previous studies, highly suggest that the temperature induced emissions at 545 nm are the same species. This is the first time that the temperature dependent red-shifted emission of ketyl and ketylimine oligofluorenes has been observed. This aside, the exact mechanism that is responsible for this emission remains contentious, especially whether the CTS is formed from intra- of intermolecular interactions.[24,87−90] For this reason, the fluorescence of **2** was examined to further aid in understanding the observed temperature dependent emission of **2**, **5**, **6**, **8**, and **9**. This was in part done by examining the concentration dependent fluorescence of **2**. A single emission was seen at 415 nm at low concentrations of **2**. This emission decreased concomitant with the formation of an emission at 545 nm with increasing concentration. The concentration dependent fluorescence is evident in Figure 6. It should be noted that the emission spectra

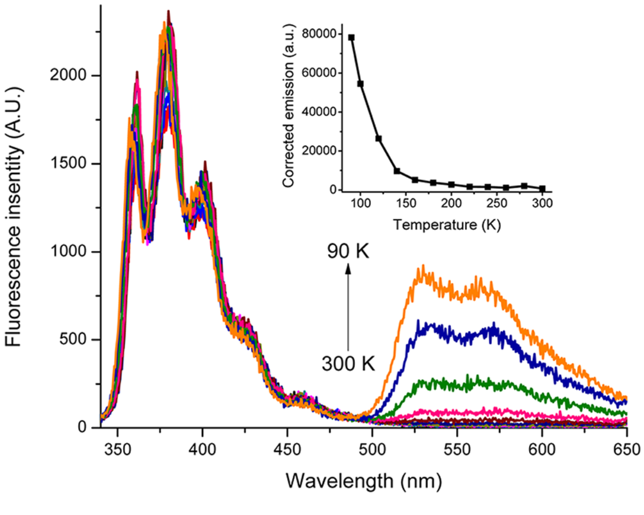


Figure 5. Fluorescence spectra of **8** uncorrected for temperature dependent refractive index change measured in a 4:1 mixture of ethanol/methanol as a function of temperature between 300 and 90 K. Inset: variation of fluorescence intensity of **8** measured at 529 nm as a function of temperature.

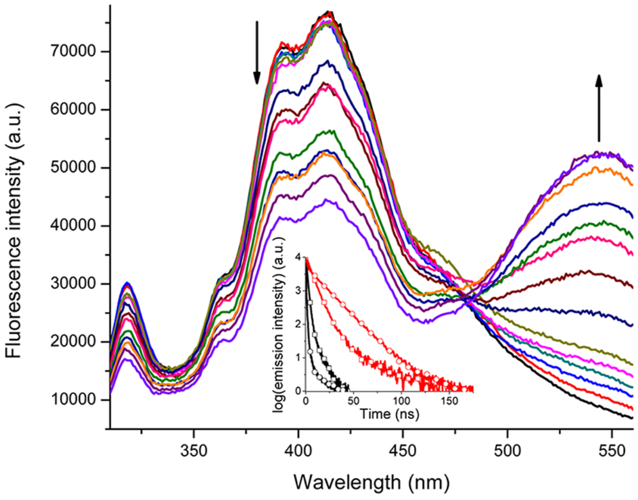


Figure 6. The fluorescence of **2** as a function of concentration in dichloromethane between 0.01 and 2.35 mM. Inset: fluorescence kinetics of **5** monitored at 423 (black line) and 500 (red line) nm at 298 (□) and 77 (○) K.

were not recorded beyond 545 nm because of interference from the excitation wavelength harmonic. Nonetheless, it is obvious from Figure 6 that the red-shifted emission from the CTS is concentration dependent and is a result of bimolecular interactions. This is in contrast to **8**, where the red-shifted emission was not observed under similar Stern–Volmer quenching conditions. In fact, the 545 nm emission was not observed even at high concentrations of **8**, i.e., with an absorbance of 4 at the excitation wavelength.

The emission kinetics of **2** and **5** were measured at 298 and 77 K to further compare the two emissions at ca. 545 nm. As seen in the inset of Figure 6, the fluorescence kinetics are not uniquely monoexponential. The kinetics of **2** at both 414 and 544 nm could be fitted to three monoexponential lifetimes, as per Table 2. While the lifetime of the fast component (<1 ns) cannot be accurately measured because it is faster than the time resolution of our instrument, the fast kinetics (<4 ns) nonetheless account for the majority of the signal (>70%). The mixed lifetimes for **2** are not surprising given the measurements were done at high concentrations to ensure the CTS emission. Fluorescence from the monomer of **2** should be temperature independent because fluorescence is an intrinsic property. In contrast, the lifetimes of the CTS should be temperature dependent with slower kinetics at reduced temperatures. The two fast components can therefore be ascribed to a singlet exciton (<1 ns) and fluorenone (3.5 ns) fluorescence, respectively.[91] Meanwhile, the longer kinetics is assigned to the CTS owing to its increased contribution that is observed at 77 K. The assignment of these species is further corroborated by previous studies.[92,93]

Table 2. Fluorescence Lifetimes Measured in Ethanol/Methanol Mixture at 298 and 77 K

		414 nm		544 nm	
		τ (ns) (% distribution)		τ (ns) (% distribution)	
compound		298 K	77 K	298 K	77 K
2	τ_1	0.9 (56)	0.8 (48)	0.4 (21)	0.5 (7)
	τ_2	3.5 (19)	3.8 (15)	1.8 (72)	7.7 (13)
	τ_3	41.3 (25)	46.6 (37)	4.5 (7)	26.9 (80)
5	τ_1		0.5 (48)		
	τ_2	1.6 (88)	1.7 (32)	1.7 (88)	1.5 (4)
	τ_3	7.9 (12)	13.3 (20)	6.3 (12)	19.6 (96)

Similar to **2**, a fast decay (ca. 1.6 ns) was observed for **5** at both wavelengths. This is assigned to the fluorene emission. While the lifetime did not vary with temperature, its contribution to the measured kinetics decreased from 88% at 298 K to 4% at 77 K. In contrast, the longer lived CTS increased in lifetime at 77 K. Similarly, the contribution of the long lifetime emission increased from 12% at 298 K to 96% at 77 K. It was further found that the Φ_{77K}/Φ_{298K} ratio for the emission of **5** centered at 425 nm was 1.85. The low concentrations ($<10^{-5}$ M) at which the fluorescence measurements were done taken together with the absence of temperature dependent red-shifted emission preclude a bimolecular process for the low temperature emission for the ketone/ketylimine derivatives. The measurements were further done in methanol, which is also a good solvent for the oligomers, and as such, their agglomeration at reduced temperature can be ignored. Sub-ps kinetic measurements would provide conclusive insight into the formation kinetics. Unfortunately, these are outside the resolution of our instrument. Nonetheless, the slight increase in the Φ_{77K}/Φ_{298K} ratio concomitant with increased contribution of the slow kinetics at the expense of the fast kinetics at reduced temperature suggests that a portion of the ketylimine/ketone oligofluorene fluorescence is quenched by CTS at room temperature. Meanwhile, the collective data nonetheless suggest that the intermediate at 545 nm is most likely a result from intramolecular CTS and not from intermolecular processes.[94,95]

CONCLUSION

The triplet quantum yields of a series of oligofluorenes and their corresponding ketone and ketylimine analogues were successfully measured by the singlet depletion method. It was found that the triplet was formed in significant amounts for the bifluorene derivatives that were substituted with a ketone or ketylimine in the 9-position. The Φ_{TT} was substantially reduced for the trifluorene derivatives. However, the ε_{TT} for these derivatives was nearly double that of their corresponding bifluorene. It was further found that a red-shifted emission, occurring at ca. 545 nm, was formed only at reduced temperature and it was concentration independent. The collective temperature, kinetics, and concentration analyses suggest that the charge transfer state is formed from intra- rather than intermolecular processes. This qualitative finding is of importance given the contention surrounding the specific origins of the green emission. It further demonstrates that vital photophysical information of polymeric systems can be derived from their oligomeric model counterparts.

ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of synthesized compounds, additional transient absorbance spectra, transient kinetic spectra, fluorescence and cryofluorescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Present Address

[†]Laboratoire de spectroscopies des matériaux, Département de Chimie, Université de Montréal, CP 6128, Centre-ville Montreal, QC.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

NSERC Canada is thanked for Discovery, Strategic Research, and Research Tools and Instruments grants allowing this work to be performed in addition to additional equipment funding from the Canada Foundation for Innovation. W.G.S. also thanks both the Humboldt Foundation and the RSC for a JWT Jones Travelling Fellowship, allowing this manuscript to be completed. A.B. thanks both NSERC and Université de Montréal for graduate scholarships. The Centre for Self-Assembled Chemical Structures is also acknowledged. The assistance of Dr. S. Dufresne and Mr. N. McGregor for preliminary contributions are appreciated.

REFERENCES

(1) Samuel, I. D. W.; Turnbull, G. A. *Chem. Rev.* **2007**, *104*, 1272.
(2) Meier, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2482.

(3) Hwang, W.; Xin, G.; Cho, M.; Cho, S. M.; Chae, H. *Nanoscale Res. Lett.* **2012**, *7*, 52/1.

(4) Xue, S.; Yao, L.; Shen, F.; Gu, C.; Wu, H.; Ma, Y. *Adv. Funct. Mater.* **2012**, *22*, 1092.

(5) Grem, G.; Martin, V.; Meghdadi, F.; Paar, C.; Stampfl, J.; Sturm, J.; Tasch, S.; Leising, G. *Synth. Met.* **1995**, *71*, 2193.

(6) Zhao, Q.; Liu, S.-J.; Huang, W. *Macromol. Chem. Phys.* **2009**, *210*, 1580.

(7) InganÄs, O.; Zhang, F.; Andersson, M. R. *Acc. Chem. Res.* **2009**, *42*, 1731.

(8) Grimsdale, A. C.; Leok Chan, K.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897.

(9) Nicolai, H. T.; Hof, A.; Blom, P. W. M. *Adv. Funct. Mater.* **2012**, *22*, 2040.

(10) Hotchkiss, P. J.; Jones, S. C.; Paniagua, S. A.; Sharma, A.; Kippelen, B.; Armstrong, N. R.; Marder, S. R. *Acc. Chem. Res.* **2012**, *45*, 337.

(11) Gather, M. C.; Köhnen, A.; Meerholz, K. *Adv. Mater.* **2011**, *23*, 233.

(12) Ma, H.; Yip, H.-L.; Huang, F.; Jen, A. K. Y. *Adv. Funct. Mater.* **2010**, *20*, 1371.

(13) Kamtekar, K. T.; Monkman, A. P.; Bryce, M. R. *Adv. Mater.* **2010**, *22*, 572.

(14) Faccinetto, A.; Mazzucato, S.; Pedron, D.; Bozio, R.; Destri, S.; Porzio, W. *ChemPhysChem* **2008**, *9*, 2028.

(15) Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. *J. Phys. Chem. B* **2004**, *108*, 8689.

(16) Chi, C.; Enkelmann, C. I. V.; Ziegler, A.; Lieser, G.; Wegner, G. *Chem.—Eur. J.* **2005**, *11*, 6833.

(17) Chi, C.; Im, C.; Wegner, G. *J. Chem. Phys.* **2006**, *124*, 024907/1.

(18) Ouyang, X.; Huo, Y.; Lu, L.; Ge, Z.; Ji, W. *Appl. Phys. A: Mater. Sci. Process.* **2011**, *105*, 891.

(19) Zhou, X.-H.; Zhang, Y.; Xie, Y.-Q.; Cao, Y.; Pei, J. *Macromolecules* **2006**, *39*, 3830.

(20) Coluccini, C.; Metrangolo, P.; Parachini, M.; Pasini, D.; Resnati, G.; Righetti, P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5202.

(21) Boiocchi, M.; Bonizzoni, M.; Moletti, A.; Pasini, D.; Taglietti, A. *New J. Chem.* **2007**, *31*, 352.

(22) Chan, K. L.; Sims, M.; Pascu, S. I.; Ariu, M.; Holmes, A. B.; Bradley, D. D. C. *Adv. Funct. Mater.* **2009**, *19*, 2147.

(23) Montilla, F.; Mallavia, R. *Adv. Funct. Mater.* **2007**, *17*, 71.

(24) Romaner, L.; Pogantsch, A.; Freitas, P. S. d.; Scherf, U.; Gaal, M.; Zojer, E.; List, E. J. W. *Adv. Funct. Mater.* **2003**, *13*, 597.

(25) Chan, K. L.; Sims, M.; Pascu, S. I.; Ariu, M.; Holmes, A. B.; Bradley, D. D. C. *Adv. Funct. Mater.* **2009**, *19*, 2147.

(26) Rathnayake, H. P.; Cirpan, A.; Karasz, F. E.; Odoi, M. Y.; Hammer, N. I.; Barnes, M. D.; Lahti, P. M. *Chem. Mater.* **2007**, *19*, 3265.

(27) He, B.; Li, J.; Bo, Z.; Huang, Y. *Polym. J.* **2007**, *39*, 1345.

(28) Pijper, T. C.; Pijper, D.; Pollard, M. M.; Dumur, F.; Davey, S. G.; Meetsma, A.; Feringa, B. L. *J. Org. Chem.* **2010**, *75*, 825.

(29) Kappaun, S.; Scheiber, H.; Trattnig, R.; Zojer, E.; List, E. J. W.; Slugovc, C. *Chem. Commun.* **2008**, 5170.

(30) Jo, J.; Vak, D.; Noh, Y.-Y.; Kim, S.-S.; Lim, B.; Kim, D.-Y. *J. Mater. Chem.* **2008**, *18*, 654.

(31) Becker, K.; Lupton, J. M.; Feldmann, J.; Nehls, B. S.; Galbrecht, F.; Gao, D. Q.; Scherf, U. *Adv. Funct. Mater.* **2006**, *16*, 364.

(32) Colombo, S.; Coluccini, C.; Caricato, M.; Gargiulli, C.; Gattuso, G.; Pasini, D. *Tetrahedron* **2010**, *66*, 4206.

(33) Dufresne, S.; Roche, I. U.; Skalski, T.; Skene, W. G. *J. Phys. Chem. C* **2010**, *114*, 13106.

(34) Pogantsch, A.; Zaami, N.; Slugovc, C. *Chem. Phys.* **2006**, *322*, 399.

(35) Chi, C.; Im, C.; Enkelmann, V.; Ziegler, A.; Lieser, G.; Wegner, G. *Chem.—Eur. J.* **2005**, *11*, 6833.

(36) Chen, R.-F.; Zheng, C.; Fan, Q.-L.; Huang, W. *J. Comput. Chem.* **2007**, *28*, 2091.

(37) Mukhopadhyay, S.; Ramasesha, S.; Guha, S. *J. Chem. Phys.* **2010**, *132*, 044104/1.

(38) Shigeta, M.; Morita, M.; Konishi, G.-i. *Molecules* **2012**, *17*, 4452.

(39) Matsushita, Y.; Ichimura, T.; Hikida, T. *Chem. Phys. Lett.* **2002**, *360*, 65.

(40) Carmichael, I.; Hug, G. L. *J. Phys. Chem.* **1985**, *89*, 4036.

(41) Carmichael, I.; Helman, W. P.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1987**, *16*, 239.

(42) Bonneau, R.; Carmichael, I.; Hug, G. L. *Pure Appl. Chem.* **1991**, *63*, 289.

(43) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(44) Pérez Guarìn, S. A.; Dufresne, S.; Tsang, D.; Sylla, A.; Skene, W. G. *J. Mater. Chem.* **2007**, *17*, 2801.

(45) Burrows, H. D.; Arnaut, L. G.; Pina, J.; Seixas de Melo, J.; Chattopadhyay, N.; Alcacer, L.; Charas, A.; Morgado, J. *Chem. Phys. Lett.* **2005**, *402*, 197.

(46) Bazin, M.; Bosca, F.; Marin, M. L.; Miranda, M. A.; Patterson, L. K.; Santus, R. *Photochem. Photobiol.* **2000**, *72*, 451.

(47) Dufresne, S.; Skalski, T.; Skene, W. G. *Can. J. Chem.* **2011**, *89*, 173.

(48) Lee, J.-I.; Klaerner, G.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1083.

(49) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 6922.

(50) Anemian, R.; Mulatier, J.-C.; Andraud, C.; Stephan, O.; Vial, J.-C. *Chem. Commun.* **2002**, 1608.

(51) Kamtekar, K. T.; Wang, C.; Bettington, S.; Batsanov, A. S.; Perepichka, I. F.; Bryce, M. R.; Ahn, J. H.; Rabinal, M.; Petty, M. C. *J. Mater. Chem.* **2006**, *16*, 3823.

(52) Lee, S. H.; Tsutsui, T. *Thin Solid Films* **2000**, *363*, 76.

(53) Murphy, R. S.; Moorlag, C. P.; Green, W. H.; Bohne, C. *J. Photochem. Photobiol., A* **1997**, *110*, 123.

(54) Andrews, L. J.; Deroulede, A.; Linschltz, H. *J. Phys. Chem.* **1978**, *82*, 2304.

(55) Gastilovich, E. A.; Korol'kova, N. V.; Val'kova, G. A. *Zh. Fiz. Khim.* **1991**, *65*, 2881.

(56) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Modern Molecular Photochemistry Of Organic Molecules*; University Science Books: 2010.

(57) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Principles of Molecular Photochemistry: An Introduction*; University Science Books: Sausalito, CA, 2009.

(58) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(59) Alam, M. M.; Ito, O.; Adam, W.; Grimm, G. N.; Saha-Möller, C. R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1851.

(60) Bourque, A. N.; Dufresne, S.; Skene, W. G. *J. Phys. Chem. C* **2009**, *113*, 19677.

(61) Barik, S.; Friedland, S.; Skene, W. G. *Can. J. Chem.* **2010**, *88*, 945.

(62) Tsang, D.; Bourgeaux, M.; Skene, W. G. *J. Photochem. Photobiol., A* **2007**, *192*, 122.

(63) Bolduc, A.; Dong, Y.; Guerin, A.; Skene, W. G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6946.

(64) Bensasson, R.; Dawe, E. A.; Long, D. A.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1319.

(65) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904.

(66) Martinez, C. G.; Neuner, A.; Marti, C.; Nonell, S.; Braun, A. M.; Oliveros, E. *Helv. Chim. Acta* **2003**, *86*, 384.

(67) Jovanovic, S. V.; Morris, D. G.; Pliva, C. N.; Scaiano, J. C. *J. Photochem. Photobiol., A* **1997**, *107*, 153.

(68) Becker, H.-D.; Burgdorff, C.; Löhmannsröben, H.-G. *J. Photochem. Photobiol., A* **1995**, *86*, 133.

(69) Biczok, L.; Berces, T. *J. Phys. Chem.* **1988**, *92*, 3842.

(70) Hunter, T. F. *Trans. Faraday Soc.* **1970**, *66*, 300.

(71) Windsor, M. W.; Dawson, W. R. *Mol. Cryst.* **1966**, *4*, 253.

(72) Heinzelmann, W.; Labhart, H. *Chem. Phys. Lett.* **1969**, *4*, 20.

(73) Amand, B.; Bensasson, R. *Chem. Phys. Lett.* **1975**, *34*, 44.

(74) Wagner-Czauderna, E.; Lipka, R.; Kalinowski, M. K. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 668.

(75) Ghosh, H. N.; Adamczyk, K.; Verma, S.; Dreyer, J.; Nibbering, E. T. J. *Chem.—Eur. J.* **2012**, *18*, 4930.

(76) Vitkup, D.; Ringe, D.; Petsko, G. A.; Karplus, M. *Nat. Struct. Mol. Biol.* **2000**, *7*, 34.

(77) Cariati, E.; Lanzeni, V.; Tordin, E.; Ugo, R.; Botta, C.; Giacometti Schieroni, A.; Sironi, A.; Pasini, D. *Phys. Chem. Chem. Phys.* **2011**, *13*, 18005.
(78) Scaiano, J. C. *CRC Handbook of Organic Photochemistry*; CRC Press: Boca Raton, FL, 1989.
(79) Carmichael, I.; Hug, G. L. Spectroscopy and Intramolecular Photophysics of Triplet States. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. *I*, p 369.
(80) Lawrence, A, S. *Tetrahedron Lett.* **1969**, *10*, 923.
(81) Monroe, B. M.; Groff, R. P. *Tetrahedron Lett.* **1973**, *14*, 3955.
(82) Hayashi, S.; Inagi, S.; Fuchigami, T. *Macromolecules* **2009**, *42*, 3755.
(83) Dias, F. B.; Macanita, A. L.; de Melo, J. S.; Burrows, H. D.; Guntner, R.; Scherf, U.; Monkman, A. P. *J. Chem. Phys.* **2003**, *118*, 7119.
(84) Ferenczi, T. A. M.; Sims, M.; Bradley, D. D. C. *J. Phys.: Condens. Matter* **2008**, *20*, 045220.
(85) Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. *J. Phys. Chem. B* **2004**, *108*, 8689.
(86) Liu, L.; Lu, P.; Xie, Z.; Wang, H.; Tang, S.; Wang, Z.; Zhang, W.; Ma, Y. *J. Phys. Chem. B* **2007**, *111*, 10639.
(87) Simas, E. R.; Gehlen, M. H.; Pinto, M. F. S.; Siqueira, J.; Misoguti, L. *J. Phys. Chem. A* **2010**, *114*, 12384.
(88) Traiphol, R.; Charoenthai, N.; Manorat, P.; Pattanatornchai, T.; Srikhirin, T.; Kerdcharoen, T.; Osotchan, T. *Synth. Met.* **2009**, *159*, 1224.
(89) Józefowicz, M.; R. H., J.; Karolczak, J.; Heldt, J. *Z. Naturforsch., A* **2003**, *58*, 144.
(90) Gadermaier, C.; Romaner, L.; Piok, T.; List, E. J. W.; Souharce, B.; Scherf, U.; Cerullo, G.; Lanzani, G. *Phys. Rev. B* **2005**, *72*, 045208.
(91) Tong, M.; Sheng, C. X.; Vardeny, Z. V. *Phys. Rev. B* **2007**, *75*, 125207.
(92) Sims, M.; Bradley, D. D. C.; Ariu, M.; Koeberg, M.; Asimakis, A.; Grell, M.; Lidzey, D. G. *Adv. Funct. Mater.* **2004**, *14*, 765.
(93) Zojer, E.; Pogantsch, A.; Hennebicq, E.; Beljonne, D.; Bredas, J.-L.; de Freitas, P. S.; Scherf, U.; List, E. J. W. *J. Chem. Phys.* **2002**, *117*, 6794.
(94) Knaapila, M.; Bright, D. W.; Nehls, B. S.; Garamus, V. M.; Almásy, L. s.; Schweins, R.; Scherf, U.; Monkman, A. P. *Macromolecules* **2011**, *44*, 6453.
(95) Dias, F. B.; Pollock, S.; Hedley, G.; Palsson, L. O.; Monkman, A.; Perepichka, I. I.; Perepichka, I. F.; Tavasli, M.; Bryce, M. R. *J. Phys. Chem. B* **2006**, *110*, 19329.