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Ultrafast Energy Transfer in Oligofluorene–Aluminum Bis(8-hydroxyquinoline)acetylacetone Coordination Polymers

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Abstract: Understanding the excited-state dynamics in conjugated systems can lead to their better utilization in optical sensors, organic photovoltaics (OPVs), and organic light-emitting diodes (OLEDs). We present the synthesis of self-assembled coordination polymers comprising two types of fluorescent moieties: discrete fluorene oligomers of a well-defined length (n = 1–9) connected via aluminum(III) bis(8-quinolinate)acetylacetone joints. Due to their well-defined structure, these materials allowed for a detailed study of energy migration processes within the materials. Thus, femtosecond transient spectroscopy was used to study the ultrafast energy transfer from the oligofluorene to the quinolinolate moieties, which was found to proceed at a rate of 1011 s−1. The experimental results were found to be in agreement with the behavior predicted according to the Beljonne’s improved Förster model of energy transfer. In addition, the solid-state and semiconductor properties of these coordination polymers allowed for the fabrication of OLEDs. Preliminary experiments with simple two- and three-layer devices fabricated by spin-coating yield bright yellow electroluminescence with maximum brightness of 6000 cd/m2, with a turn-on voltage of ~6 V and a maximum external quantum efficiency of up to 1.2%, suggesting their potential for use in PLED applications.

Introduction

Excited-state resonance energy transfer1 plays a pivotal role in numerous natural processes including the photosynthesis,2 imaging, and diagnostics,3 as well as in various applications such as (bio)chemical sensing,4 photovoltaics,5 and organic light-emitting devices (OLEDs).6 In conjugated polymers,7,8 energy transfer and exciton migration processes are very efficient and therefore can be exploited in amplifying sensors response,9,10 exciton migration toward dissociation zones in solar cells,11,12 and controlling the output of OLEDs.13 Recently, the mechanisms of energy (exciton) migration in conjugated systems have been widely investigated in order to better understand their electronic properties,14,15 which are of fundamental interest not only from an academic viewpoint but also because of their use in real-life applications.

In general, the theoretical analysis of energy migration in conjugated polymers requires advanced models to account for the significant exciton delocalization and to estimate the electronic coupling between neighboring fragments. One of the examples was reported by Beljonne et al who developed an improved Förster formalism to describe the energy transfer between polyindeno fluorene and perylene dye endcaps. In this work, exciton hopping rates were estimated and the transient photoluminescence was simulated qualitatively to describe the energy transfer process. However, strict predictions of the exciton dynamics in conjugated polymers are very complicated due to the irregular distribution of energy donor (D) and acceptor (A) sites arising from partial loss of electronic coupling due to static nature of the conformational processes, as well as potential traps resulting from structural defects introduced during their preparation. The structural inhomogeneities in conjugated polymers such as chain defects or kinks are difficult to detect by analytical techniques, but may still substantially limit the electronic communication taking place in the polymer. Conjugated materials with well-defined donor–acceptor (D–A) distances studied by Meijer et al. are of significant advantage for studies of energy migration in hydrogen-bonded supramolecular structures of different sizes that combine the electronic properties of well-defined oligomers with the processability of polymeric structures. However, energy transfer in these hydrogen-bound systems has been studied only by steady-state methods lacking the time-resolved characterization. To provide a detailed insight into the energy migration mechanism in conjugated systems and the time scale of exciton migration in self-assembled structures that combine donor and acceptor moieties at well-defined distances, fluorene oligomers (n = 1–9) connected via aluminum(III) bis(8-quinolinolato) acetylacetonate complexes were synthesized (see Chart 1). The evolution of the energy transfer rate with an increasing oligofluorene length was compared to the prediction of the model put forward by Beljonne, and experimental evidence to support the theoretical treatment of singlet exciton migration in rigidly linked conjugated systems is provided. Compared to the energy transfer in solution, the solid-state studies revealed slightly different properties to the solution behavior. This insight was used in the preparation of simple OLEDs. Overall, the present results highlight the potential of self-assembled conjugated-coordination polymers as models for energy transfer studies, as well as a new class of functional conjugated materials.

Results and Discussion

Synthesis. A limited number of coordination polymers were demonstrated to display electroluminescence. These were self-assembled polymers in which the zinc atoms have been used to template the assembly of organic ligands into coordination polymers.

We decided to utilize an 8-hydroxyquinoline (HQ, oxinate)–AlIII mediated self-assembly synthetic approach for the construction of well-defined bichromophoric systems la–e. In order to avoid the formation of dendritic structures around the octahedral geometry of the aluminum center, a 2,4-pentanedionate (acetylacetone, acac) ancillary ligand was introduced. Moreover, the presence of acac ligands in the coordination sphere of aluminum quinolinolates has been reported to be beneficial for the electroluminescence performance of Alq.

We found that two acetylacetone ligands can be selectively replaced from Al(acac)3 by 8-hydroxyquinoline under mild conditions to afford the heteroleptic complex, bis(8-quinolinate)(acetylacetone)aluminum(III), Alq2(acac), in high yield (see Scheme 1). We presumed that reaction of Al(acac)3 with ditopic ligands of the general structure HQ-(fluorene)-HQ would afford polymeric materials driven by coordination to aluminum centers. Thus, the coordination polymers la–e were prepared by self-assembly of the HQ-(fluorene)-HQ ditopic ligands in the presence of Al(acac)3 in toluene (see the Supporting Information for synthetic details). The polymers were characterized by 1H NMR and GPC analysis, which confirmed the polymeric nature of the materials (Mn = 6.1–42.1 kDa, 12 repeating units on average). As expected, the coordination polymers la–e were soluble in a range of common organic solvents such as dichloromethane, toluene, chloroform, and tetrahydrofuran.

The ditopic ligands utilized for the synthesis of coordination polymers la–e were synthesized according to the published procedure using selective desymmetrization of the oligofluorene structure by monolithiation to introduce the trimethylsilyl (TMS) protecting group, 26, 27-iodo-desilylation by ICl ipso-substitution of the protecting TMS group, 26, 27 palladium-catalyzed preparation of fluorene boronic acid esters, 28 palladium-catalyzed cross-couplings, and deprotection of the benzyl


Figure 1 shows the assignment of the aromatic signals in 1H NMR spectra of the synthesized building blocks.

Optical Properties of the Bichromophoric Coordination Polymers. The formation of the coordination polymers results in establishing two distinctly different chromophores: the conjugated arylene backbone and the Alq2(acac) complex, both showing distinct spectroscopic behavior. The UV-visible absorption spectra of the coordination polymers 1a–e were recorded at room temperature in CH2Cl2 and are shown in Figure 2. The spectra showed contributions of both the aluminum quinolinolate and oligofluorene (OF) chromophores, with the former becoming less prominent as the oligofluorene absorption increased with length.

Interestingly, the UV-visible absorption spectra of 1a–e also showed behavior typical for extended conjugated species. Specifically, the π-π* absorption band corresponding to the aluminum quinolinolate moiety (λmax = 388 nm, 3.20 eV)31 is shifted to lower energy for 1a–e (405 nm, 3.06 eV), indicating extended conjugation in these ligands. Similarly, the absorption bands

Figure 2. UV–vis absorption spectra of 1a–e in a CH2Cl2 solution showing contribution of both oligofluorene (OF) and AlIII quinolinolate chromophores.

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of the oligofluorene chromophores are red-shifted compared to the values reported for unsubstituted oligomers of the same length. For the system bearing one fluorene unit 1a, the π→π* absorption is centered at 327 nm (3.79 eV) while fluorene exhibits a maximum at 301 nm (4.11 eV).32 For 1b with three fluorene units, a π→π* absorption maximum is located at 362 nm (3.43 eV) while terfluorene shows an absorption peak centered at about 350 nm (3.54 eV).32,33 As the length of the oligofluorene fragment is increased, the differences in energy for the S₀→S₁ transition of 1a–e and the corresponding unsubstituted oligofluorenes are reduced. This behavior suggested relatively weak participation of the quinolinolate groups in the overall conjugation of the longer systems 1d and 1e (Table I).

Intramolecular energy transfer from the oligofluorene fragments to Alq₃(acac) moieties was observed in the steady-state emission spectra of 1a–e in solution. In the materials 1a–b comprising one and three fluorene units, respectively, only the emission from the quinolinolate units (~550 nm) was detected regardless of the excitation wavelength (Figure 3, left). Excitation of the coordination polymers 1c–e (n = 5–9) at 340 nm (mostly π→π* oligofluorene) resulted in two emission components centered at 410 and 550 nm (3.02 and 2.25 eV). These features are consistent with S₁→Sₙ transitions from oligofluorene fragments and aluminum quinolinolate moieties, respectively. As one could expect, the emission corresponding to the oligofluorene becomes more prominent with an increasing number of fluorene units. This is explained by increased probability of populating conformational states with reduced conjugation along the oligofluorene backbone due to rotation around fluorene-fluorene bonds.

The excitation spectra of 1a–e monitored at 550 nm (Figure 3, right) fully resembled the UV–visible absorption spectra suggesting reasonably effective migration of singlet excitons from oligofluorene bridges to the Alq₃(acac) moieties. This premise was further supported by the major contribution of the Alq₃-type fluorescence in the emission spectra, despite the significant length of the ligands (19–85 Å) and their high fluorescence quantum yield (ΦFl ≈ 0.9–1.0).34 It was reasoned that the energy transfer must compete very effectively with the fast radiative decay of oligofluorene (τFl = 400–800 ps).35,36 Presumably as a result of exciton delocalization between both fluorophores. This possibility was further investigated by femtosecond UV–visible transient absorption spectroscopy.

Ultrafast Energy Migration in 1a–e. To monitor the energy transfer process in 1a–e, we studied the spectral and kinetic features of each chromophore upon selective excitation. Thus, two model systems, aluminum(III) tris(5-phenyl-8-quinolinolate) (2) and terfluorene end-capped with trimethylsilyl groups (3), were studied first (Figure 4A). Upon excitation of 2 at 475 nm (2.61 eV, π→π* of Alq₃), positive absorption centered approximately at 520 nm along with a second feature of lower intensity between 540–760 nm were observed (Figure 4C). After its initial rise, the intensity of this spectrum did not decay significantly within the time window of the experiment (1.6 ns). Given the relatively long lifetime of this species, the observed transient spectrum was attributed to a transition of the singlet state S₁→Sₚ. This was further confirmed by monitoring this spectrum by transient UV–visible spectroscopy in a nanosecond regime as well as by the photoluminescence decay kinetics (τFl = 9.72 ns).31

Excitation of the oligofluorene model 3 at 340 nm (3.65 eV, π→π* of oligofluorene) resulted in broad absorption ranging between 475–760 nm after a quick initial rise (0.2 ps). Stimulated emission was also detected in the region of 400–475 nm as a negative signal (Figure 4D). The decay of this transient at 750 nm showed a monoeXponential behavior with lifetime (τ ≈ 642 ± 4 ps), which agreed with the reported fluorescence lifetimes for terfluorene obtained from up-conversion fluorescence studies.36 Furthermore, the observed spectral features are in excellent agreement with literature reports of the absorption of singlet excited-state of oligofluorene,37 which confirmed the nature of the oligofluorene excited state.

The considerable overlap between the spectral features of aluminum quinolinolate and oligofluorene required careful comparison of the transient spectra obtained for systems 1a–e. Excitation of the coordination polymers 1a–e under the same conditions employed for 2 (λexc = 475 nm, 1.5 mW) afforded the transient spectra displayed in Figure 5 (0.2 ps after a rise). The kinetics of these transients followed the behavior observed for the model 2, thus confirming the selective formation of the singlet excited-state in the Alq₃-type moieties. Beside the absorption at 520 nm, a new band (λmax = 575–640 nm) was observed in the spectra of 1a–e. This band shifted toward lower energies and increased in intensity with a higher number of fluorene units, suggesting that quinolinolate→oligofluorene conjugation affected the spectrum of the excited state. Interestingly, the absorption maximum in 1c–e with 5, 7, and 9 fluorene units, respectively, did not show a significant red shift compared to 1b with only three fluorene units. This leveling off in the red-shift of the fluorene transient maxima suggests that regardless of the oligomer length the effect of conjugation is not significantly extended beyond three units.

Upon excitation of the oligofluorene moiety in 1a–e under the same conditions employed for the terfluorene model system 3 (λexc = 340 nm, 0.5 mW), distinct transient spectra are observed (Figure 5, right). The shape of the spectra differed

| Table 1. Summarized Absorption Data for Bichromophoric Systems 1a–e |
|---------------------------------|-----------------|-----------------|
| system | n (fluorene units) | λmax [Å] | ΔE (eV)* |
| 1a | 1 | 327 [6.4 × 10³, 405 [2.2 × 10⁴] | 0.19 |
| 1b | 3 | 362 [9.1 × 10⁴] | 0.11 |
| 1c | 5 | 372 [1.3 × 10⁴] | 0.07 |
| 1d | 7 | 375 [4.1 × 10⁴] | 0.02 |
| 1e | 9 | 376 [5.1 × 10⁴] | 0.00 |

* Difference in energy for the S₀→S₁ transition between unsubstituted oligofluorenes and 1a–e.27,35

dramatically in the series 1a–e depending on the length of the oligofluorene segment. For systems 1a–b (n = 1, 3) the spectra were essentially identical to transients observed upon excitation at 475 nm, suggesting a strong electronic coupling. The high degree of coupling observed for 1a–e is consistent with the excited-state being distributed all over the two chromophores. Transient spectra of 1c–e (n = 5–9) comprised features attributable to both Alq₃ and the oligofluorene. Flattening of the band centered at 640 nm, a shift of the maximum of absorption to higher wavelengths, and the stimulated emission from oligofluorene were detected at early times (τ < 10 ps) and were replaced by the features observed upon excitation at 475 nm (Figure 6). After the spectral evolution, the decay of the transients of 1a–e also exhibited a long-lived state (τ ≥ 1.6 ns) attributed to the Alq₃-type singlet excited state. In summary, the observed transient spectra support the hypothesis

of efficient singlet energy transfer from oligofluorene to aluminum quinolinolate in these bichromophoric systems.

The observed spectral evolution allowed for assessment of the rate constant of the energy transfer process (Figure 6, right). Because of the significant change in intensity at 750 nm, this wavelength was selected for monitoring the kinetics of the energy transfer in 1c–e (see Appendix, Supporting Information for additional spectra). The rate constant of the energy transfer from oligofluorene to aluminum quinolinolate was calculated using the equation:

$$k_{ET} = \frac{1}{\tau_{Obs}} - \frac{1}{\tau_{Fl}}$$

where $k_{ET}$ is the overall rate of energy transfer, $\tau_{Obs}$ is the lifetime observed for the spectral change in the transient experiment, and $\tau_{Fl}$ represents the fluorescence lifetime of the energy donor in the absence of the acceptor. In all cases, very short lifetimes corresponding to ultrfast energy transfer rate constants were obtained. A summary of the calculated values for the energy transfer rates is presented in Table 2. In all cases the estimated efficiency of energy transfer is above 99%, which is in agreement with the

![Figure 5. Left: Transient absorption spectra of 1a–e 0.2 ps after excitation at 475 nm (1.5 mW). The dotted line indicates the saturation of the peak absorption around 640 nm. Right: Transient absorption spectra of 1a–e 0.2 ps after excitation at 340 nm (0.5 mW).](image)

![Figure 6. Left: Transient absorption spectra for 1d after excitation at 340 nm (0.5 mW) at various times. Right: Exponential fit of the kinetic profile at 750 nm.](image)

![Table 2. Calculated Rate Constants for Energy Transfer in the Coordination Polymers 1c–e Monitored by Decay at 750 nm](image)

<table>
<thead>
<tr>
<th>System</th>
<th>$n$ (fluorene units)</th>
<th>$\tau_{Obs}$ (ps)</th>
<th>$\tau_{Fl}$ (ps)</th>
<th>$k_{ET}$ ($s^{-1}$) $\times 10^{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>5</td>
<td>1.45 ± 0.05</td>
<td>549</td>
<td>6.9 ± 0.2</td>
</tr>
<tr>
<td>1d</td>
<td>7</td>
<td>1.40 ± 0.05</td>
<td>505</td>
<td>7.1 ± 0.2</td>
</tr>
<tr>
<td>1e</td>
<td>9</td>
<td>2.99 ± 0.08</td>
<td>476</td>
<td>3.3 ± 0.1</td>
</tr>
</tbody>
</table>

The lifetime values were adapted from the literature.

results recorded in the steady state experiments (≥98%, see Supporting Information for details).

**Comparison of the Experimental Results with the Improved Förster Theoretical Model.** The exciton dynamics observed for systems 1a–e were found to be in excellent agreement with the improved Förster formalism reported for description of energy transfer in this type of conjugated systems.\(^{14b}\) According to the model, when a conjugated oligomer acts as an energy donor, the intramolecular energy transfer process consists of multistep exciton migration along the chain. This mechanism results in virtual shortening of the distance between the donor and acceptor, as well as a corresponding increase of the ultrafast energy transfer rates. The results from both steady-state photoluminescence and time-resolved absorption spectroscopy experiments confirm that the light absorption by the oligofluorene fragments in 1a–e is followed by an ultrafast exciton migration (\(k_{\text{ET}} = 3.3 - 7.1 \times 10^{11} \text{s}^{-1}\)) toward aluminum quinolinolate moieties of lower energy (Figure 7).

In general, the energy transfer rates in wirelike conjugated species are governed by the actual donor–acceptor spectral overlap and HOMO–LUMO levels, as well as the donor–acceptor electronic coupling, which depends on their actual distance. Figure 7 shows three examples of materials 1c–e that differ in the three features above. Interestingly, the overall energy transfer rates (\(k_{\text{ET}}\)) found experimentally (Table 2) are 6.9 ± 0.2 × 10^{11}, 7.1 ± 0.2 × 10^{11}, and 3.3 ± 0.1 × 10^{11} s\(^{-1}\) for D−A distances of 52, 68, and 85 Å, respectively. Here, the \(k_{\text{ET}}\) is composed of two components corresponding to the exciton hopping between the fluorene moieties (\(k_{\text{eh}}\)) and the one corresponding to the strongly exothermic transfer from fluorene to Al\(^{III}\) quinolinolate (\(k_{\text{f}}\)). While the fluorene-to-quinolinolate transfer is always exothermic and fast, the exciton hopping between the fluorene displays more complex energetics (Figure 7) and is likely to be a decisive factor to influence the final \(k_{\text{ET}}\).

The fact that the initial increase of 16 Å in the D−A distance between 1c and 1d is accompanied by an actual increase in energy transfer rate is rationalized in terms of the model put forward by Beljonne et al.\(^{14b}\) which suggests that maximum rates for exciton hopping are observed for shorter donor and acceptor fragments (2−3 indenofluorene moieties corresponding to ca. three fluorene units). When the donor and acceptor size increases beyond those of “optimal conjugation lengths”, the rates for exciton hopping decrease making the overall energy transfer process less efficient (i.e., \(k_{\text{ET}}\) is decreased). This assertion is based on the fact that the energy transfer requires both the spectral overlap of the decoupled donor/acceptor fragments as well as some degree of electronic coupling between them. In the material 1c with five fluorene units (Figure 7A), the optimal donor (central terfluorene) is flanked by two single fluorene units. While the emission of the terfluorene donor is 390−450 nm, the absorption of single fluorene is in the deep UV. Thus, the forward exciton hopping (\(k_{\text{eh}}\)) is disfavored by an insufficient orbital overlap. The corresponding energy diagram shows the same feature in terms of the energies of the respective singlet excited states and the activation energy required for exciton hopping, which renders the energy transfer in 1c less efficient. Needless to say, this particular distribution of fluorene moieties in 1c shown in Figure 7A is not the only one possible but is the one most likely responsible for the relatively lower rate (\(k_{\text{ET}} = 6.9 ± 0.2 \times 10^{11} \text{s}^{-1}\)) in energy transfer in 1c according to the model.\(^{14b}\)

In the “intermediate” material 1d, the terfluorene donor with “optimal conjugation length” is flanked with two acceptor moieties composed of two fluorene moieties that display a sufficient spectral overlap and require only moderate activation energy for forward exciton hopping (\(k_{\text{eh}}\)) from the donor to the

\[ E = k_{\text{ET}}(k_{\text{eh}} + \tau_F^{-1}), \]

**Figure 7.** Schematic representation of the mechanism for intramolecular energy transfer as proposed for the behavior of the bichromophoric systems 1c–e. Only one pathway of energy migration is shown for simplicity purposes.
between the polymer chains rather than to the increased degree of interchain energy transfer pathways due to a close contact effective than intrachain energy transfer, which is limited by statistical probability of obtaining one singlet exciton per three nonradiatively decaying triplet excitons.

Preliminary incorporation of the coordination polymers into OLEDs was performed by processing the materials by spin-coating. Simplified OLED architectures ITO/PEDOT:PSS(500 Å)/1a–c(600 Å)/CsF(10 Å):Al(1200 Å) were fabricated in order to confirm the electroluminescent abilities of these hybrid materials. Devices based on 1a–c (n = 1–3) exhibited somewhat similar performance, suggesting the ability of these materials to transport both electrons and holes in an efficient manner. Overall, the maximum luminance was 6000 cd/m² with a turn-on voltage of ~6 V and a maximum external quantum efficiency of 0.4%. An improved quantum efficiency and higher luminance was obtained when a bathocuproin (BCP) hole-blocking layer was vapor-deposited on top of the emissive polymer. The resulting device displayed saturated yellow emission (CIE coordinates X = 0.440, 0.255; Figure 8) and external quantum efficiency of 1.2%. On the basis of the comparison with the previously published data describing metalpolymers OLEDs based on phosphorescent metallocomplexes, these results from the simple unoptimized fluorescence-only devices are encouraging. This is particularly true if one considers that due to the quantum statistics of electron–hole recombination, the fluorescence-only devices are believed to have an upper theoretical efficiency limit of ca. 25% due to the statistical probability of obtaining one singlet exciton per three nonradiatively decaying triplet excitons.

Conclusions

Novel coordination polymers comprising oligofluorene moieties of a varying size (n = 1–9) connected via aluminum(III) bis(8-quinolinolate)acetylacetonate (Alq,(acac)) complexes were synthesized and their photophysical properties were studied. Due to the bichromophoric nature of the polymers stemming from the oligofluorene and quinolinolate moieties, these materials display interesting photonic behavior. Thus, the singlet energy transfer in these coordination polymers was investigated by transfer in these coordination polymers was investigated by...
steady-state techniques and time-resolved absorption spectroscopy in the femtosecond regime. Strong electronic coupling between the chromophores is evidenced by the single spectral behavior of materials comprising shorter oligofluorene fragments 1a–b (n = 1, 3). For materials 1c–e with longer oligofluorene segments (n = 5, 7, and 9), spectral features from both quinolinolate and oligofluorene chromophores were observed. The energy migration from oligofluorene to the quinolinolate moieties was observed proceeding at a rate order of 10^{11} \text{s}^{-1}. The exact determination of energy transfer rates was possible by the well-defined discrete structure and purity of the building blocks, which could be purified to achieve high purity because of their small-molecule nature. The energy transfer behavior described for systems 1a–e was rationalized according to the theoretical model proposed by Beljonne for the treatment of exciton migration in rigidly linked conjugated polymer systems. These results represent clear experimental evidence to support this model for intramolecular singlet–singlet energy transfer.

In the solid state, complete energy transfer from oligofluorene fragments to the quinolinolate centers was observed due to intermolecular energy transfer. Preliminary experiments with simple two- and three-layer devices fabricated by spin-coating yield bright yellow electroluminescence with maximum brightness of 6000 cd/m² with a turn-on voltage of ∼6 V, and a maximum external quantum efficiency of up to 1.2% suggesting their potential in PLED applications. These results may open up the possibility of controlling not only the emission color but also the semiconducting properties of novel materials by balancing charge transport through well-defined conjugated fragments.

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Supporting Information Available: General methods, synthesis and characterization of 1a–e, X-ray crystallographic data (CIF file) of Alq2acac, additional optical spectra, quantitative analysis of the steady-state PL, and fabrication of the OLEDs. This material is available free of charge via the Internet at http://pubs.acs.org.

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