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Self-Location of Acceptors as "Isolated" or "Stacked" Energy Traps in a Supramolecular Donor Self-Assembly: A Strategy to Wavelength Tunable FRET Emission

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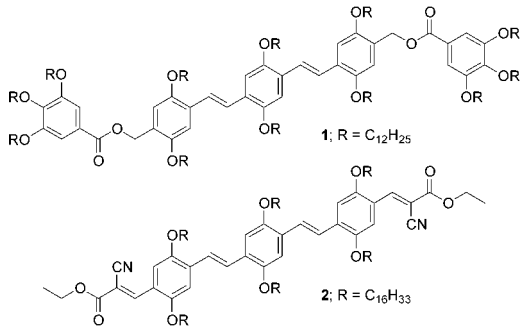
The present communication describes the design of a supramolecular light harvesting assembly with tunable emission (100 nm red shift). The motivation for this work stems from two seminal reports by Meijer and co-workers[1] and Desvergne and co-workers,[2] who independently observed that higher concentration of the acceptor in a supramolecular environment results in complex energy transfer (ET) processes. However, a systematic investigation remains elusive mainly due to the problems associated with the conflict of the photophysical properties of the donor−acceptor system and the competing direct excitation of the acceptor. To overcome these limitations of supramolecular light harvesting assemblies, a rational choice of the donor−acceptor motifs and their self-organization are extremely important. As a proof-of-principle, we reveal the controlled placement of an acceptor either as "isolated" or "aggregated" energy traps of different HOMO−LUMO gaps within a supramolecular donor scaffold that exhibits efficient antenna effect resulting in the continuous shift of the fluorescence resonance energy transfer (FRET) emission from green to red.

There are reports pertaining to systems where ET occurs from aggregates to monomers[1−3] and aggregates to aggregates.[4] In many such cases, organogelators,[2,5,6] dendrimers,[7] and conjugated polymers[8] have been used as supramolecular scaffolds. However, control of energy transfer from self-assembled donors to monomers and aggregates of the acceptor has not been successfully demonstrated so far. A combination of these two processes would provide a pathway for wavelength tunable emission upon a single wavelength excitation. The success of such a goal lies in the judicious selection of the donor and acceptor building blocks with ideally suited optical and self-assembly properties. We have chosen compounds **1** and **2** as the donor and the acceptor, respectively, since the optical properties of these molecules satisfy most of the requirements of an ideal supramolecular ET system.[2,8e,9] In addition, these molecules form organogels,[10] thereby providing a conducive supramolecular scaffold that facilitates the FRET process. These molecules were synthesized by standard procedures and were characterized by NMR, IR, and MALDI-TOF mass spectrometry analyses.[11]



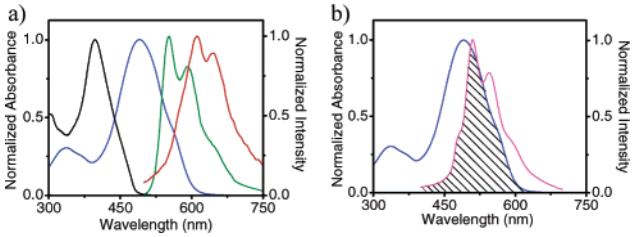


Figure 1. (a) Absorption spectra of **1** (black), **2** (blue), and fluorescence spectra of **2** at 50 °C (green) and at 20 °C (red). (b) Spectral overlap of the emission of **1** (magenta) and the absorption of **2** (blue) in decane ($c = 3 \times 10^{-4}$ M, $l = 1$ mm, $\lambda_{ex} = 380$ nm for **1** and 480 nm for **2**).

The UV/vis absorption and emission properties of **1** and **2** in the gel state (3×10^{-4} M in decane) are shown in Figure 1. There is a difference of 94 nm between the absorption maximum of **1** and **2** in decane at 20 °C. The quantum yields of fluorescence (Φ_f) for solutions of **1** and **2** in decane at 20 °C (quinine sulfate as standard for **1** and rhodamine 6G for **2**) were 0.38 and 0.12, respectively. Variable temperature absorption and emission properties of **1** and **2** (3×10^{-4} M) revealed aggregation of the molecules in decane.[11] At 20 °C, the emission of **2** in decane showed a maximum at 610 nm which is assigned to the aggregate species, whereas at 50 °C, the emission maximum occurred at 552 nm that corresponds to the monomer species. Aggregation of **2** is also clear from the concentration-dependent emission studies (Figure S3).[11] The emission of **1** and the absorption of **2** showed significant spectral overlap integral ($J(\lambda) = 1.78 \times 10^{15}$ M^{-1} cm^{-1} nm^4) (Figure 1b). It must be noted that the acceptor **2** has minimum absorption at the λ_{max} of the donor **1**, thus minimizing the direct excitation of the acceptor. These properties of **1** and **2** are ideal for the FRET between these molecules.

Excitation of **1** at 380 nm in the presence of 0−2 mol % of **2** resulted in gradual decrease in the emission ($\lambda_{max} = 509$ nm) of the former with the concomitant formation of the monomer emission ($\lambda_{max} = 555$ nm) of the latter. However, coassemblies with 2−20 mol % of **2** showed gradual shift of the emission toward long wavelength, eventually resulting in the aggregate emission of **2** (Figure 2a). Thus, a continuous red shift of the emission from 509 to 610 nm ($\Delta\lambda = 101$ nm) could be possible by simply varying the concentration of the acceptor, resulting in ca. 98% quenching of the monomer emission with a rate of 1.73×10^{10} s^{-1}. This rate is comparable with that reported for the ET in other supramolecular systems[12] and is an indication of fast exciton migration.[8a,f] Fluorescence lifetime decay profiles ($\lambda_{ex} = 375$ nm) monitored at the aggregate emission maximum of **1** (509 nm) showed shortening of the decay profile with increasing concentration of **2** (Figure 2b). The accelerated decay of the donor fluorescence in the presence of **2** rules out any trivial ET pathways. The excited donor self-assembly

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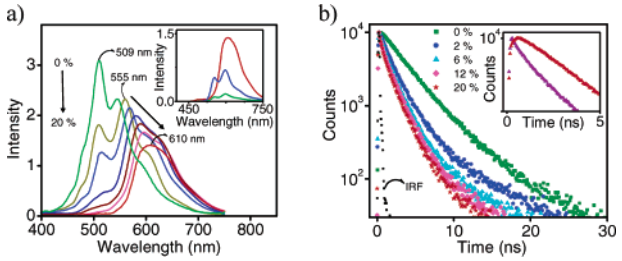

Figure 2. (a) Fluorescence emission ($\lambda_{ex} = 380$ nm) and (b) lifetime decay profiles ($\lambda_{ex} = 375$ nm, monitored at 509 nm) of **1** on addition of different amounts of **2** (0−20 mol %). The insets show (a) comparison of FRET emission with 20 mol % of **2** excited at 380 nm (red), upon direct excitation of **2** in the absence of **1** excited at 490 nm (blue) and at 380 nm (green), (b) comparison of the decay profiles of **2** in the presence (red) and in the absence (purple) of **1** monitored at 610 nm ($c = 3 \times 10^{-4}$ M, $l = 1$ mm).

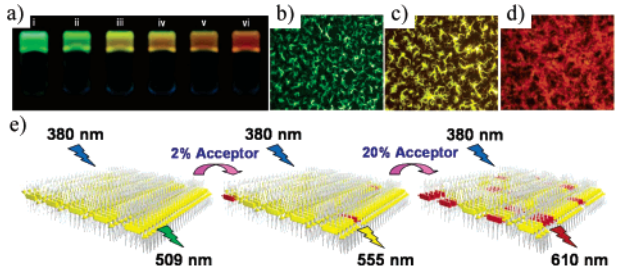

Figure 3. (a) Photographs of the gels of **1** and **2** at different compositions of **2** (i) 0 mol %, (ii) 1 mol %, (iii) 2 mol %, (iv) 6 mol %, (v) 12 mol %, and (vi) 20 mol % under illumination at 365 nm. (b, c, and d) Fluorescence microscopy images of the drop-casted films from decane solution of **1** ($c = 3 \times 10^{-4}$ M) in the presence of 0, 2, and 20 mol %, respectively, of **2** (40× magnification). (e) Schematic representation of the FRET process within the coassemblies having different amounts of the acceptor.

efficiently transfers the energy to the acceptors thus populating the excited states of the latter before it decays by radiative mechanism.[1,13] This is clear from the comparison of the fluorescence decay of **2** alone with that of the coassembly (20 mol % of **2**, Figure 2b, inset). The growth observed for the coassembly at short time scales is associated with the initial population buildup of the excited states of **2** upon energy transfer from the donor singlet which is followed by the decay.[13] Comparison of the fluorescence spectra of **2** in the presence ($\lambda_{ex} = 380$ nm) and in the absence of **1** ($\lambda_{ex} = 490$ nm) under identical experimental conditions reveals 2-fold increase in the intensity of the FRET emission (Figure 2a, inset). Due to the low extinction coefficient at 380 nm, direct excitation of **2** during ET is negligible as evidenced by the extremely weak fluorescence.

Photographs and the fluorescence microscopy images of the coassembled gels of **1** and **2** under different compositions allow direct visualization of the FRET process (Figure 3). In the absence of **2**, the donor **1** exhibits a bright green emission. On adding different amounts of **2** (0−20 mol %), the emission color changes from green to red through yellow and orange.

The reason for the shift in the emission of **1** in the presence of varying amounts of **2** is depicted in Figure 3e. Coassembly of **1** and **2** facilitates gel formation and controlled self-location of the latter within the self-assembly of the former in decane. Under low mol %, **2** exists as isolated monomers within the coassembly. At this stage, partial transfer of the excitation energy occurs to the monomer of **2** resulting in yellow emission ($\lambda_{max} = 555$ nm). In contrast, under higher mol % of **2**, the statistically distributed aggregates with a different HOMO−LUMO gap provide an energy gradient resulting in the funneling of the excitation energy to higher order aggregates of **2**. Thus, a gradual red shift of the emission toward 610 nm occurs with a complete quenching of the donor emission. It must be noted that this phenomenon is not possible if the acceptor does not self-organize in a controlled way within the coassembly or if ultrafast energy transfer occurs with very low mol % of the acceptor, resulting in complete quenching of the donor emission. The success of the present approach is the subtle balance between these two processes by the rational selection of the donor and acceptor.

In conclusion, the self-location of an acceptor as an isolated or aggregated energy trap within the self-assembly of a gel-forming donor in a controlled manner resulted in FRET with tunable emission. The approach to supramolecular light harvesting assembly described here allows the continuous shift of the emission from green to red upon a single wavelength excitation.

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Supporting Information Available: Details of synthesis, characterization, and experimental procedures. Absorption and emission studies, XRD, AFM, and gelation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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