Donor–Acceptor Systems: Energy Transfer from CdS Quantum Dots/Rods to Nile Red Dye

Suparna Sadhu and Amitava Patra*[a]

We demonstrate strong evidence of shape-dependent efficient resonance energy transfer between CdS quantum dots (QDs) and quantum rods (QRs) (donor) to Nile Red dye (acceptor). We also report a simple solution-based method for the preparation of high quality CdS QDs and CdS QRs at relatively low temperature. The observed quenching of PL intensities are 78.8% and 63.8% for CdS QDs and QRs, respectively in the presence of Nile Red dye. The calculated energy-transfer efficiencies are 45% and 19% from QDs and QRs to dyes, respectively. The energy transfer varies with changing the shape of the nanoparticles. The estimated Förster distances ($R_0$) are 37.8 and 33.8 Å for CdS QDs and QRs, respectively. In the present study, the estimated distances ($r$) between one donor and one acceptor are 39.1 and 43.1 Å for QDs and QRs, respectively, using the efficiency of Förster resonance energy transfer (FRET) which depends on the inverse sixth power of the distance of separations between one nanocrystal and one dye molecule. Considering single donor and multiple acceptors interactions, the calculated average distances ($r_0$) between the donor and acceptor are 47.7 and 53.9 Å for QDs and QR’s, respectively. The steady-state and time-resolved spectroscopic analysis of nanoassemblies confirm the formation of one donor and multiple acceptors.

1. Introduction

Research in the field of quantum dot (QD)-based fluorescence energy transfer is of great current interest as there are many potential applications in the areas of luminescence tagging, imaging, medical diagnostics, multiplexing and most recently in biosensors.[1–4] As these potential applications are still very much in the design-phase, further fundamental research in the field of QD-based fluorescence energy-transfer remains a challenge. It is now well established that quantum dots (QDs) are ideal for fluorescence resonance energy-transfer based devices due to their narrow emission and broad excitation spectra.[1–4] Furthermore, the large size of QDs compared to organic dyes also provides the design of such configuration where multiple acceptors can interact with a single donor, which enhances the efficiency and thus increases the sensitivity.[1] Recently, Schleinbaum et al.[10] reported the configuration of one donor dye interacting with multiple acceptor dyes. Medintz et al.[10] reported the potential of luminescent semiconductor quantum dots for development of hybrid inorganic-bio receptor sensing materials. They demonstrated the use of luminescent CdSe–ZnS QDs as energy donors in fluorescence resonance energy-transfer based assays with organic dyes as energy acceptors in QD–dye labeled protein conjugates. Burda et al.[10] observed non-Förster type energy-transfer behavior in QD-phthalocyanine conjugates and they also reported the surface effects on QD-based energy-transfer.[11] In most cases, the energy transfer in QD conjugates is discussed as a Förster-resonance type energy-transfer (FRET) process. FRET is a powerful method to determine the distance between donor and acceptor fluorophores. Dyes are commonly used in biological system for FRET study.[11] The FRET studies are commonly used for biological research to measure the molecular distances or donor-to-acceptor proximity. FRET occurs through the dipole-dipole interactions between an excited donor (D) molecule and an acceptor (A). Mattoussi et al.[12] have already discussed that for QD-based FRET analysis, point-dipole interaction may not be appropriate because nanocrystals have finite size and are relatively large compared to the dye molecules. So far, the analysis by FRET method is the best available method for QD-based system. The efficiency of FRET does not only depend on the distance of separation between donor and acceptor molecules. According to the Förster theory[13], the rate of energy transfer is given by Equation (1)

$$k_r(r) = \frac{1}{\tau_0} \left( \frac{R_0}{r} \right)^6$$

(1)

where τ₀ is the lifetime of the donor in the absence of the acceptor, $r$ is the distance between the donor and acceptor, and $R_0$ is known as the Förster distance—the distance at which the transfer rate $k_r(r)$ is equal to the decay rate of the donor in absence of the acceptor. The Förster distance ($R_0$) is defined[14] by Equation (2)

$$R_0^2 = \frac{9000(ln10)\chi^2\phi_0}{128\pi^3 N_m^2} \int_0^{\infty} F_D(\lambda)F_A(\lambda)\lambda^4 d\lambda$$

(2)

where $\phi_0$ is the quantum yield of donor in the absence of the acceptor, $N$ is the Avogadro’s number, $n$ is the refractive index of the medium. $F_D(\lambda)$ is the corrected fluorescence intensity of the

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donor in the wavelength range from \( \lambda \) to \( \lambda + \Delta \lambda \), with the total intensity normalized to unity, \( e_A(\lambda) \) is the extinction coefficient of the acceptor at \( \lambda \) (units of \( \text{m}^{-1} \text{cm}^{-1} \)) and \( k^2 \) is the orientation factor of 2 dipoles interacting and is usually assumed to be equal to 2/3.

We have already reported in our previous study\(^{13}\) that the shape of Au nanoparticles influences the energy transfer from Rhodamine 6G to Au nanoparticles. To the best of our knowledge, shape-dependence energy transfer from CdS nanocrystals to Nile Red dye, is not found in the literature. It is known that the dipole moment depends on the surface reconstruction therefore it varies with changing the shape and size of the nanoparticles. Thus, different shapes might effect the energy-transfer process. Guyot-Sionnest and co-workers\(^{14}\) demonstrated that the dipole moment of CdSe nanocrystals scales linearly with the crystallite diameter. Furthermore, Alivisatos et al.\(^{15}\) showed the permanent dipole-moment of CdSe nanorods increases linearly with volume. Therefore, there is plenty of scope for understanding the effect of shape of nanocrystals on the fluorescence energy-transfer. Herein, we try to address the following issues; how the efficiency of energy transfer, and donor–acceptor distance vary with changing the shape of the nanoparticles. The influence of the shape of the nanoparticles on the energy-transfer from QDs to Nile Red dye is studied by steady-state and time-resolved spectroscopy.

2. Results and Discussion

Figures 1a and b show the TEM images and the size distribution of particles of the as-prepared CdS nanosphere and nanorod, respectively. Results reveal uniform spherical nanocrystals with an average diameter \( 3.1 \pm 0.2 \) nm (inset of Figure 1a) and nearly mono-disperse uniform nanorod having an average length \( 13.2 \pm 0.4 \) nm and diameter \( 5.8 \pm 0.3 \) nm and the average aspect ratio is 2.3 (inset in Figure 1b).

2.1. Steady-State Study

Figures 2a and b display the absorption spectrum of CdS nanocrystals and normalized absorption spectrum of Nile Red dye and photoluminescence (PL) spectrum of CdS for two sets of donor–acceptor used. The overlap functions defined as

\[
J(\lambda) = \int_0^\infty F_D(\lambda) e_A(\lambda) \lambda^2 d\lambda
\]

are shown in the inserts, where \( F_D(\lambda) \)

is the normalized emission spectrum of the donor (CdS), \( e_A(\lambda) \)

is the absorption coefficient of the acceptor (Nile Red dye) at wavelength \( \lambda \) (in nm). The absorption spectrum of Nile red dye shows peaks centered at 487 and 507 nm and the PL peaks are at 472 and 478 nm for CdS nanoparticle (QDs) and nanorod (QRs), respectively, under excitation at 370 nm. As shown in Figure 2, the absorption spectrum of the dye overlaps with the emission spectrum of CdS nanocrystals. Generally, FRET rates depend strongly on the overlap between donor emission and acceptor absorption spectra and the spectral overlap is constant for a given donor–acceptor system. However, Pons et al.\(^{16}\) demonstrated that the size heterogeneity effects the spectral overlap on the FRET between QD donors and proximal dye acceptors. Nile Red dye has negligible absorption at 370 nm,
therefore the CdS QDs–dye and CdS QRs–dye complexes were excited at this wavelength in order to excite the QDs and QRs selectively. It is known from the previous study[2] that van der Waals type interactions between CdS nanocrystals and dye molecules contribute to the binding of the energy acceptor to the nanocrystal’s surface. A quenching in PL intensity of QDs and QRs emission is observed in the presence of the dye molecule (Figures 3a and b). The steady-state energy-transfer efficiency is calculated from Equation (3).

\[
\phi_{ET} = 1 - \frac{I_{DA}}{I_D}
\]  

(3)

where \(I_D\) and \(I_{DA}\) are the relative integrated intensities of the donor emission in the absence and presence of the acceptor. The observed PL quenching intensities are 78.8% and 63.8% for CdS QDs and QRs, respectively. This PL quenching process is due to energy transfer from QDs to the dyes. Results indicate that the quenching of PL varies with changing the shape of the nanocrystals. To understand the quenching process, the measurement of fluorescence intensity with varying quencher (dye) concentration (2.0 \(\times 10^{-6}\) m to 16.0 \(\times 10^{-6}\) m) is important. A gradual quenching of the fluorescence intensity of QDs and QRs with increasing the concentration of dye (quencher) is shown in Figures 3a and b. Pons et al.[16] reported a systematic decrease in QD PL with an increasing acceptor-to-QD ratio per conjugate. Dayal et al.[17] have found a decrease in PL intensity with increasing dye concentration, and larger wavelengths are quenched more than the shorter wavelengths due to increasing self-absorption with increasing dye concentration. The inset of Figure 3 showing the shift to shorter wavelengths of the emission spectrum with increasing quencher concentrations, which is consistent with earlier reports.[16, 18] Pons et al.[16] described this emission band shift as due to a modification of the population distribution. Kamat et al.[18] also reported a blue shift in the absorption maximum upon addition of Rhodamine 6G to the gold nanoparticles and concluded that the dimeric aggregates are of H-type. The emission spectra of the quenched CdS is calculated from taking the difference between the unquenched and quenched emission spectra.[11] The quenched residues show an emission maximum at 476 nm (for QDs) and 479 nm (for QRs). However, the unquenched residues display an emission maximum at 467 nm (QDs) and 474 nm (QRs). Results reveal that energy transfer occurs from CdS nanocrystals to the dyes. Peng et al.[5] demonstrated the energy transfer between CdTe and cy3-dyes. Lian et al.[9] also reported the energy transfer between CdS and Rhodamine B dyes. Possible pathway for the quenching of QDs excitons is the energy transfer from conduction band of CdS to the unoccupied molecular orbital of dyes, which produces an excited-state dye and CdS in its ground state.[9]

2.2. Time-Resolved Fluorescence Study

Lifetime measurements are more sensitive than PL quenching efficiencies which have errors from the fluctuations in the lamp intensity. The interaction of dyes with QDs and QRs can be monitored by their effect on the exciton lifetime, which is measured by time-correlated single-photon counting (TCSPC). We used pulsed excitation (375 nm) to measure the decay times of these QDs and QRs at their maximum fluorescence. Figures 4a and b show the time-resolved fluorescence decay curves of CdS QDs and QRs without and with Nile Red dye solution. Herein, all PL decay profiles are well described by three-exponential functions using Equation (9), although the fitting to tri-exponential functions proved sometimes problematic. Lian et al.[9] already demonstrated the tri-exponential decay of CdS nanocrystals during energy transfer from CdS to Rhodamine B. The photoluminescence decay of CdS QDs is tri-exponential with decay components of (\(\tau_1\) 313 ps (2.15%), (\(\tau_2\) 2.95 ns (9.44%)) and (\(\tau_3\) 22.89 ns (88.41%)) and the average decay time is 22.62 ns (Table 1), using Equation (10). However, the average decay time of CdS QRs is 12.43 ns in presence of dyes. The average decay time of CdS QRs is 19.51 ns and 15.76 ns in the absence and presence of dyes, respectively (Table 1). It clearly reveals that there is a shortening of the decay time of nanocrystals in the presence of dyes which is one of the hallmarks of efficient FRET between donor–acceptor molecules.[11] The exciton lifetime decreases in the presence of dyes, suggesting the quenching of excitons in QDs and QRs by the dye molecules. The Stern–Volmer relationship between the quenching of excited states and the quencher concentration is given by Equation (4)[19]

\[
\text{tau} = \frac{\tau_0}{1 + K_{SV}[Q]} = 1 + K_{SV}[Q]
\]  

(4)
where \( t_0 \) and \( t \) are the lifetimes in the absence and presence of quencher, respectively. \( K_{SV} \) is the Stern–Volmer quenching constant and \([Q]\) is the concentration of the quencher. The dye concentration varies from 2 to 16 \( \mu \)M, because the Stern–Volmer theory is only valid for dilute solutions. The Stern–Volmer plot of \( t_0/t \) versus quencher concentration is given in Figure 5 and curves downward towards the x-axis, indicating the difference in accessibility of CdS nanocrystals to the quencher dye. Therefore, a modified Stern–Volmer equation [Eq. (5)] is considered to determine the fraction of accessible residue and the Stern–Volmer quenching constant. Equation (5) allows \( f_a \) and \( K_a \) to be determined graphically (inset of Figure 5). A plot of \( t_0/t \) versus \( 1/[Q] \) yields \( f_a/K_a \) as the intercept and \( (f_aK_a)^{-1} \) as the slope. The intercept represents the extrapolation to infinite quencher concentration (\( 1/[Q] = 0 \)). At high quencher concentration only the inaccessible CdS are fluorescent. From the modified Stern–Volmer plot, the fraction of accessibilities are 0.25 and 0.77 for QDs and QRs respectively, and the value of \( K_a \) is \( 0.083 \times 10^{12} \) \( \text{M}^{-1} \) and \( 0.219 \times 10^{12} \) \( \text{M}^{-1} \) for QDs and QRs respectively. Results reveal that the fraction of accessibilities is higher in rod samples than spherical particle samples because of their shape. The lifetime \( t_0 \) of CdS QDs and QRs are 22.62 ns and 19.51 ns, and the estimated rate constants \( K_q \), are \( 3.66 \times 10^{12} \) \( \text{M}^{-1} \text{s}^{-1} \) and \( 11.22 \times 10^{12} \) \( \text{M}^{-1} \text{s}^{-1} \) for QDs and QRs respectively. The expected value for diffusion-controlled bimolecular rate constant is \( 10^{10} \) \( \text{M}^{-1} \text{s}^{-1} \). As the obtained value of quenching constant \( K_q \) is higher than the expected quenching constant \( (10^{10} \text{M}^{-1} \text{s}^{-1}) \), we conclude that this is not a diffusion-controlled bimolecular reaction. The energy transfer efficiency from QDs to the dye is calculated using Equation (6).

\[
\phi_{ET} = 1 - 
\]

where \( \tau_{DA} \) and \( \tau_D \) are the decay times of CdS in the presence and absence of dye, respectively. The calculated energy-transfer efficiencies from QDs and QRs to the dye are 45% and 19%, respectively (Table 2). As the energy-transfer efficiency is

**Table 1.** Decay parameters for CdS QDs and QRs without and with Nile Red dye in n-hexane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. of Nile Red Dye [( \mu )M]</th>
<th>( \chi^2 )</th>
<th>( \tau_1 ) [ns]</th>
<th>( \tau_2 ) [ns]</th>
<th>( \tau_3 ) [ps]</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( \alpha_3 )</th>
<th>( \tau ) [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CdS QD</td>
<td>0</td>
<td>1.151</td>
<td>2.95</td>
<td>22.89</td>
<td>313</td>
<td>9.44</td>
<td>88.41</td>
<td>2.15</td>
<td>22.62</td>
</tr>
<tr>
<td>1.82 ( \mu )M CdS QD</td>
<td>6</td>
<td>1.118</td>
<td>1.09</td>
<td>12.92</td>
<td>819</td>
<td>24.67</td>
<td>64.55</td>
<td>10.78</td>
<td>12.43</td>
</tr>
<tr>
<td>Pure CdS QR</td>
<td>0</td>
<td>1.092</td>
<td>3.14</td>
<td>20.82</td>
<td>404</td>
<td>29.15</td>
<td>58.52</td>
<td>12.32</td>
<td>19.51</td>
</tr>
<tr>
<td>1.82 ( \mu )M CdS QR</td>
<td>6</td>
<td>1.079</td>
<td>2.43</td>
<td>16.78</td>
<td>326</td>
<td>28.48</td>
<td>57.91</td>
<td>13.61</td>
<td>15.76</td>
</tr>
</tbody>
</table>

Figure 4. Time-resolved fluorescence decay curves of CdS QDs (A) and QRs (B) without and with Nile Red dye solution.

Figure 5. Stern–Volmer plots of A) QDs and B) QRs. Inset: modified Stern–Volmer plots.
higher in QDs than QRs, this clearly indicates that the energy transfer from nanocrystals to dyes varies with changing the shape of the nanocrystals, which may be due to different electrostatic polarizations resulting from different dipole moments. Gugot-Sionnest and co-workers\cite{14} demonstrated that the dipole moment of CdSe nanocrystals scales linearly with the crystallite diameter. Furthermore, Alivisatos et al.\cite{15} showed that the permanent dipole moment of CdSe nanorods increases linearly with volume. The average aspect ratio of a nanorod sample is 2.3. Therefore, they are known to have polarized emission which is dependent upon axis orientation. Further investigation is required to understand the issue. We estimate the overlap integral \[ \rho_n \] from the overlap of emission spectra of donor (QDs and QRs) and absorption spectra of the acceptor (dye). The overlap integral, \[ \rho_n \] values are \( 2.804 \times 10^{-14} \) and \( 2.401 \times 10^{-14} \) m\(^{-1}\)cm\(^{-1}\)nm\(^{-4}\) for CdS QDs and QRs, respectively (Table 2). The linear dependence of the energy-transfer efficiency on the spectral overlap integral (Figure 6) indicates a Förster-type energy-transfer process. The small change in the overlap integral may be due to either a small change in the emission peak and/or size homogeneity of the nanoparticle as shown in Figure 1. Pons et al.\cite{16} described the advantage of the size heterogeneity on the effects of the spectral overlap on the FRET between QD donors and proximal dye acceptors (in a QD-protein-dye conjugate). They report that the same acceptor may have different donor–acceptor spectral overlaps, due to their size heterogeneity. We estimate the distance \( r_0 \) between donor and acceptor using the FRET method as, 37.8 and 33.8 Å for CdS QDs and QRs, respectively (Table 2). Goponik et al.\cite{20} reported the Förster distance \(~ 3–3.5 \) nm between CdTe and Rhodamine B dye. Bavendi et al.\cite{21} reported the same order of magnitude for high efficient FRET between NCs of different sizes. Mattoussi and co-workers\cite{22} reported the Förster distance in the range 42–55 Å for QD with peptide/dye conjugates. In the present study, the estimated distances \( r \) between nanocrystals and dyes are 39.1 and 43.1 Å for QDs and QRs, respectively (Table 2), considering one donor and one acceptor interaction, using the efficiency of FRET (Eq. (1)).

Figures 7a and b show the efficiency of the energy transfer as a function of the ratio between the molar concentrations of donors and acceptor \( x = C_D/C_A \) in hexane. It is clearly seen from Figure 7a that the efficiency of the quenching process increases monotonically with decreasing in \( x \). It is noteworthy that the very effective quenching of QDs characterized by \( E = 0.45 \) is observed for assemblies with \( x \) equal to 0.302. It reveals that one donor QD nanocrystal assemblies with 3 acceptor dye molecules. But in case of QRs (Figure 7b), the transfer efficiency directly depends on the number of acceptor molecules adjacent to a donor molecule where transfer rates are additive in nature. In this case, the maximum quenching \( E = 0.57 \) is observed at \( x = 0.046 \). It reveals that one donor QRs nanocrystal assemblies with 22 acceptors dye molecules due to the larger surface area of QR nanocrystal which can accommodate more acceptor molecules. It is believed that the arrangement of dye molecules is different because the average aspect ratio of nanorod sample is 2.3. In case of the QRs the transition dipole moment is different for the two axes. This could lead to different transfer efficiencies, depending on whether the dye molecules are bound to the long or the short axis, while the nature of the actual chemical bond is identical. Further work is necessary to understand the effect of dipole strengths on the energy-transfer efficiency. In the case of QD nanocrystals, three acceptor molecules are associated with each QD nanocrystal in a centro-symmetric arrangement whereas 22 acceptor molecules are associated with each QR nanocrystal with non-centro-symmetric arrangement. For such complex interactions, the efficiency \( E \) can be expressed as \( E = \frac{nE_0}{n + 1} \), where \( r_{ni} \) is the average donor–acceptor distance and where \( n \) is the ac-

<table>
<thead>
<tr>
<th>System</th>
<th>( \lambda_{em} ) [nm]</th>
<th>( J/\lambda ) [m(^{-1})cm(^{-1})nm(^{-4})]</th>
<th>( \rho_n )</th>
<th>( E ) [%]</th>
<th>( r_0 ) [Å]</th>
<th>( r ) [Å]</th>
<th>( r_{ni} ) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS QD (1.82 µm)</td>
<td>472</td>
<td>2.804 \times 10^{-14}</td>
<td>0.63</td>
<td>45</td>
<td>37.8</td>
<td>39.1</td>
<td>47.7</td>
</tr>
<tr>
<td>CdS QR (1.82 µm)</td>
<td>478</td>
<td>2.401 \times 10^{-14}</td>
<td>0.38</td>
<td>19</td>
<td>33.8</td>
<td>43.1</td>
<td>53.9</td>
</tr>
</tbody>
</table>

\[ \text{[a] Time-resolved study, } E = \frac{nE_0}{n + 1}, \text{where } r_{ni} = \frac{R_{ni}}{R_{ni} + R_D + R_A} \]
The calculated average distances \( r \) between the donors and acceptors are 47.7 and 53.9 Å for QDs and QRs, respectively (Table 2). The distance between donor–acceptor varies with changing the shape of the nanocrystals. The short distance between donor–acceptor indicates the efficient energy-transfer from donor (QDs/QRs) to the acceptor (Nile Red dye).

### Experimental Section

**Materials:** Oleylamine (70%, Aldrich), Cadmium acetate (Merck) and Sulfur powder were used as received. Nile Red dye (Aldrich) was used as acceptor for energy transfer study. The structure of Nile Red dye is shown in Scheme 1. The spectroscopic grade solvents (n-hexane, toluene, methanol and ethanol) were used for optical study.

**Preparation of CdS nanoparticle (QD):** Colloidal solution of CdS nanocrystals were prepared by a slightly modified method developed by Joo et al.\(^{(23)}\). 0.133 gm (0.5 mM) cadmium acetate in 5 mL oleylamine was heated to 150 °C under Ar flow for 20 min to form a clear solution. Separately, an oleylamine-sulfur solution was prepared by dissolving 0.016 g m (0.5 mM) of sulfur powder in 2.5 mL of oleylamine and quickly injected into the above hot reaction mixture under gentle stirring. The reaction mixture was kept at the desired growth temperature (150 °C). After 8 hrs the reaction is quenched by the addition of a large volume of anhydrous toluene into the reaction mixture. The nanocrystals were separated from the toluene solution by the addition of ethanol and centrifuged. The yellow precipitate was then re-dispersed in n-hexane. For optical studies, the excess ligand and reaction precursors were removed by repeated precipitation and centrifugation.

**Preparation of CdS nanorods (QR):** For the preparation of CdS nanorods, the ratio of cadmium and sulfur precursor was taken as 1:3. 0.133 gm (0.5 mM) cadmium acetate in 5 mL oleylamine was heated to 150 °C under Ar flow for 20 min to form a clear solution. An oleylamine-sulfur solution (dissolving 0.048 g m (1.5 mM) of sulfur powder in 2.5 mL of oleylamine) quickly injected into the above hot reaction mixture under gentle stirring. The reaction mixture was kept for 6 hrs at the desired growth temperature (150 °C). The growth of the CdS nanocrystals was terminated as before and the excess ligands and reaction precursors were removed by extensive purification prior to optical studies.

**Characterization of CdS Nanocrystals:** The transmission electron microscopy (TEM) images were taken using a JEOL-TEM-2010 transmission electron microscope operating voltage at 200 kV to analyze the shape, size, size distribution and structure of the resulting nanocrystals. Samples for TEM were prepared by making a clear solution of samples in n-hexane and placing a drop of the solution on a carbon coated copper grid.

**Optical Measurements:** All optical measurements were carried out promptly (within 24 hr after the synthesis) on samples in order to minimize re-absorption and avoid absorption saturation. Absorption and fluorescence spectra of CdS QD’s and QR’s samples in n-hexane (spectroscopic grade) solution were obtained at room temp-
temperature with a Shimadzu UV-2450 UV/Vis spectrometer and a Horiba Jobin Yvon FluoroMax-P fluorescence spectrometer, respectively. Photoluminescence quantum yields (QY) were obtained by comparison with standard dye (Coumarine 500 in methanol), using Equation (7)\(^{(24)}\)

\[
QY_s = \frac{F_s \times A_s \times n_s^2 \times QY_s}{F_r \times A_r \times n_r^2}
\]

(7)

where \(F_s\) and \(F_r\) are the integrated fluorescence emission of the sample and the standard, respectively. \(A_s\) and \(A_r\) are the absorbance at the excitation wavelength of the sample and the reference, respectively, and \(QY_s\) and \(QY_r\) are the quantum yields of the sample and the reference (\(QY_r = 90\%\)\(^{(25)}\)), respectively. The refractive indices of the solvents in which the sample and reference are prepared are given by \(n_s\) (1.426) and \(n_r\) (1.375) respectively. The values of \(F_s\) and \(F_r\) are determined from the photoluminescence spectra corrected for the instrumental response, by integrating the emission intensity over the desired spectral range. Only the band-edge luminescence peak was integrated (any other luminescence bands, such as defect associated luminescence or solvent fluorescence were discarded as background). For the time-correlated single-photon counting (TCSPC) measurements, all samples were excited at 375 nm using a picosecond diode laser (IBH Nanoleo-07) in an IBH Fluorocube apparatus. The pulse duration is about 200 ps. The repetition rate is 500 KHz. The fluorescence decays were collected at a Hamamatsu MCP photomultiplier (C487802). The fluorescence decays were analyzed using IBH DAS6 software. Equation (8) was used to analyze the experimental time-resolved fluorescence decays, \(P(t)\):

\[
P(t) = b + \sum^n_{i=1} a_i \exp\left(-t/t_i\right)
\]

(8)

Here, \(n\) is the number of discrete emissive species, \(b\) is a baseline correction ("dc" offset), and \(a_i\) and \(t_i\) are the pre-exponential factors and excited-state fluorescence lifetimes associated with the \(i\)th component, respectively. For multi-exponential decays (\(n\), the average decay time, \(\langle t \rangle\), was calculated from Equation (9)

\[
\langle t \rangle = \sum^n_{i=1} a_i t_i^2 / \sum^n_{i=1} a_i t_i
\]

(9)

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