Electronic Supporting Information

Contrasting Tunability of Quinizarin Fluorescence with \( p \)-Sulfonatocalix[4,6]arene Hosts

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Figure S1. Job plots for (A) SCX4-QZ and (B) SCX6-QZ systems obtained from the changes in the fluorescence intensities on complex formation.
<table>
<thead>
<tr>
<th>Concentration of SCX4 (mM)</th>
<th>$\tau_1$ (ns)</th>
<th>$A_1$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$A_2$ (%)</th>
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<td>-</td>
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<td>22.7</td>
<td>1.1</td>
<td>88</td>
<td>1.4</td>
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The fluorescence decays are fitted by considering either single or bi-exponential functions; with general expression as, $I(t) = \sum a_i \exp(-t/\tau_i)$. The relative contribution of each decay component $\tau_i$, is calculated as, $A_i = a_i \tau_i / \sum a_i \tau_i$. Here $a_i$ is the absolute pre-exponential factor for the $i^{th}$ decay component.
**Table S2.** Fluorescence decay parameters\(^a\) for QZ (9 μM) in the presence of different SCX6 concentrations. \(A_1\) and \(A_2\) correspond to the relative contributions of the two lifetime components, \(\tau_1\) and \(\tau_2\), in the bi-exponential analysis of the decays.

<table>
<thead>
<tr>
<th>Concentration of SCX6 (mM)</th>
<th>(\tau_1) (ns)</th>
<th>(A_1) (%)</th>
<th>(\tau_2) (ns)</th>
<th>(A_2) (%)</th>
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<td>22.5</td>
<td>0.55</td>
<td>26</td>
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</table>

\(a\) The fluorescence decays are fitted by considering either single or bi-exponential functions; with general expression as, \(I(t) = \sum a_i \exp(-t/\tau_i)\). The relative contribution of each decay component \(\tau_i\), is calculated as, \(A_i = a_i \tau_i / \sum a_j \tau_j\). Here \(a_i\) is the absolute pre-exponential factor for the \(i^{th}\) decay component.

**Note S1.**

Calculations for the radiative and nonradiative rate constants and quenching rate constants of SCX4-QZ and SCX6-QZ systems

The excited state lifetimes of QZ in the free and host bound states are expressed as follows:

\[
\tau_{\text{free}} = \frac{1}{k_f + k_{nr}}
\]

(1)
Here \( k_f \) and \( k'_f \) are the radiative rate constants, \( k_{nr} \) and \( k'_{nr} \) are the total nonradiative rate constants (excluding the quenching rate by SCXn) in the free and bound state of the dye respectively, and \( k_q \) is the quenching rate constant for the bound QZ due to the electron transfer (ET) or charge transfer (CT) interaction with the SCXn hosts.\(^1\)

For QZ in ethanol solution, the reported fluorescence lifetime (\( \tau_f \)) is 2.1 ns, radiative rate constant (\( k_f \)) is \( 5.2 \times 10^7 \) s\(^{-1} \) and the nonradiative rate constant (\( k_{nr} \)) is \( 4.2 \times 10^8 \) s\(^{-1} \).\(^2\) From the experimentally determined fluorescence lifetime of QZ in water, and considering that the radiative rate constant of the dye is similar in ethanol and water, the nonradiative rate constant of QZ in water is estimated using equation 1, as \( 6.6 \times 10^8 \) s\(^{-1} \).

Since QZ binds very loosely to the wide SCX6 cavity, it is quite reasonable to assume that for the SCX6-QZ system, \( k_f = k'_f \) and \( k'_{nr} \approx k_{nr} \). Therefore, from the measured fluorescence lifetime of the SCX6-QZ complex (0.6 ns; cf. Table S2) the \( k_q \) value for SCX6-QZ can be readily calculated from equation 2 as \( 9.6 \times 10^8 \) s\(^{-1} \).

Using this \( k_q \) value for SCX6-QZ, the \( k_q \) value for the SCX4-QZ system can be assumed to be about \( 6.4 \times 10^8 \) s\(^{-1} \) (i.e. \([4/6] \times 9.6 \times 10^8\) s\(^{-1} \)), based on the reasoning that SCX6 posses six electron donating \( p \)-hydroxybenzenesulfonate units while SCX4 has only four. From the measured lifetime of the SCX4-QZ complex (1.1 ns; cf. Table S1) and the calculated \( k_q \) value (\( 6.4 \times 10^8 \) s\(^{-1} \)), one can have the following relation to be justified for the SCX4-QZ system,

\[
k'_{f(SCX4•QZ)} + k'_{nr(SCX4•QZ)} = (\tau_{SCX4•QZ}^{-1} - k_q) = 2.6 \times 10^8 \text{ s}^{-1}
\]  

Further, the ratio of the quantum yields for SCX4-QZ and QZ is given as,

\[
\frac{\phi_{SCX4•QZ}}{\phi_{QZ}} = \frac{k'_{f(SCX4•QZ)}\tau_{SCX4•QZ}}{k_f(QZ)\tau_{QZ}}
\]  

From the maximum value of the intensity enhancement that is observed for the SCX4-QZ system (cf. Figure 2A), the ratio of the quantum yields for the free dye and SCX4-QZ complex is determined to be 2.04. Thus, from the known values of \( k_f \), \( \tau_{QZ} \) and \( \tau_{SCX4•QZ} \), the \( k'_{f(SCX4•QZ)} \) value is calculated to be \( 13.5 \times 10^7 \) s\(^{-1} \), which is much higher than the \( k_f(QZ) \) value of \( 5.2 \times 10^7 \) s\(^{-1} \) for free QZ.

Accordingly, \( k'_{nr(SCX4•QZ)} = 1.3 \times 10^8 \) s\(^{-1} \) and \( \Delta k_{nr} = (k'_{nr}-k_{nr}) = -5.2 \times 10^8 \) s\(^{-1} \).\(^5\)

These estimates evidently suggest that for the SCX4-QZ system not only the nonradiative rate
constant largely decreases but also the radiative rate constant substantially increases due to dye-host inclusion complex formation. Due to these changes both in the radiative and non radiative rate constants in the opposite way and due to the involvement of the quenching process by the host molecule, the steady state fluorescence intensity and fluorescence lifetime of SCX4-QZ complex shows a contrasting effect, i.e. the former increases but the latter decreases, as observed experimentally.

**Note S2.**

**Calculation of binding constants for SCXn-QZ systems**

Considering that the dye (QZ) and the host (SCXn) interact to form 1:1 host-guest complex (SCXn•QZ) through a reversible process, the formation equilibrium can be presented as,

\[ \text{SCXn + QZ} \rightleftharpoons \text{SCXn} \cdot \text{QZ} \]  

(6)

For this equilibrium, if \( K_{eq} \) is not very large, one can simply apply the condition that total host concentration \([\text{SCXn}]_0 >> [\text{SCXn} \cdot \text{QZ}]\). Thus, from the definition of the equilibrium constant, \( (K_{eq}) \), we can write,

\[ K_{eq} = \frac{[\text{SCXn} \cdot \text{QZ}]}{[\text{QZ}][\text{SCXn}]} = \frac{[\text{SCXn} \cdot \text{QZ}]}{[\text{QZ}]_0[\text{SCXn}]_0 - [\text{SCXn} \cdot \text{QZ}]} \approx \frac{[\text{SCXn} \cdot \text{QZ}]}{[\text{QZ}]_0 - [\text{SCXn} \cdot \text{QZ}][\text{SCXn}]_0} \]  

(7)

or, \([\text{SCXn} \cdot \text{QZ}] = K_{eq}[\text{QZ}]_0[\text{SCXn}]_0 - K_{eq}[\text{SCXn} \cdot \text{QZ}][\text{SCXn}]_0 \)  

(8)

or, \( \{1 + K_{eq}[\text{SCXn}]_0\}[\text{SCXn} \cdot \text{QZ}] = K_{eq}[\text{QZ}]_0[\text{SCXn}]_0 \)  

(9)

or, \( \frac{[\text{SCXn} \cdot \text{QZ}]}{[\text{QZ}]_0} = \frac{K_{eq}[\text{SCXn}]_0}{1 + K_{eq}[\text{SCXn}]_0} \)  

(10)

and \( \frac{[\text{QZ}]}{[\text{QZ}]_0} = 1 - \frac{[\text{SCXn} \cdot \text{QZ}]}{[\text{QZ}]_0} = 1 - \frac{K_{eq}[\text{SCXn}]_0}{\{1 + K_{eq}[\text{SCXn}]_0\}} = \frac{1}{\{1 + K_{eq}[\text{SCXn}]_0\}} \)  

(11)

Further, if it is considered that \( C_{QZ} \) and \( C_{\text{SCXn} \cdot \text{QZ}} \) are the relative percentage contributions of QZ and SCXn•QZ in the observed fluorescence decay, then we have,

\( C_{QZ} + C_{\text{SCXn} \cdot \text{QZ}} = 100 \)  

(12)

It is understandable that the individual contributions \( C_{QZ} \) and \( C_{\text{SCXn} \cdot \text{QZ}} \) will be proportional to their respective relative populations. Hence we can write,
\[ C_{QZ} = k_{QZ} \frac{[QZ]}{[QZ]_0} \]  

(13)

and \[ C_{SCXn\cdot QZ} = k_{SCXn\cdot QZ} \frac{[SCXn\cdot QZ]}{[QZ]_0} \]  

(14)

where \( k_{QZ} \) and \( k_{SCXn\cdot QZ} \) are the respective proportionality constants that would be the functions of their fluorescence yields as well as the absorption coefficients at the excitation wavelength for the respective lifetime components. Therefore, following equations 10 and 11 we can have,

\[ C_{SCXn\cdot QZ} = \frac{k_{SCXn\cdot QZ} K_{eq}[SCXn]_0}{1 + K_{eq}[SCXn]_0} \]  

(15)

and \[ C_{QZ} = \frac{k_{QZ}}{1 + K_{eq}[SCXn]_0} \]  

(16)

References
