Electronic Supporting Information

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

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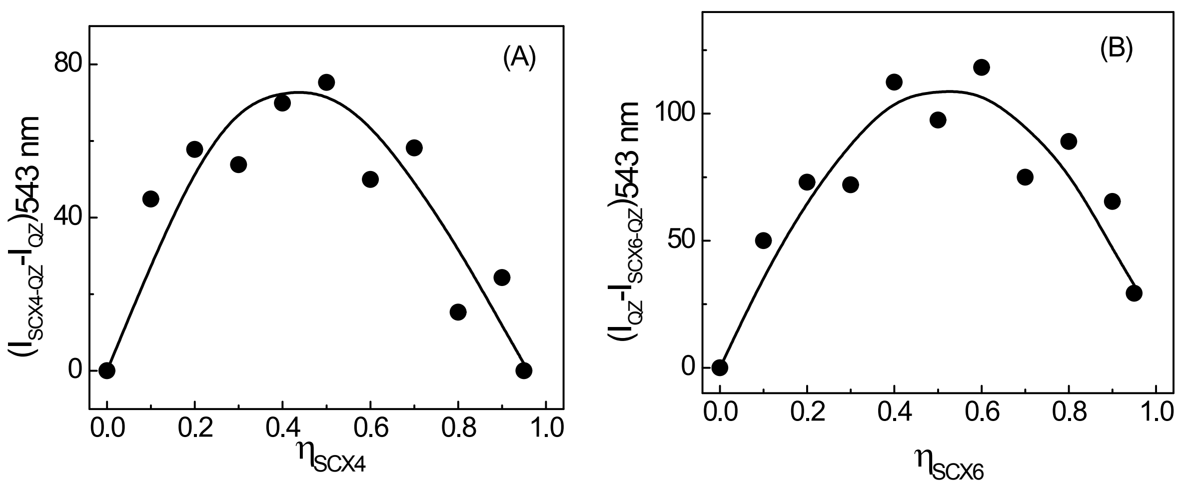

Figure S1. Job plots for (A) SCX4-QZ and (B) SCX6-QZ systems obtained from the changes in the fluorescence intensities on complex formation.

Table S1. Fluorescence decay parameters[a] for QZ (9 μM) in the presence of different SCX4 concentrations. A_1 and A_2 correspond to the relative contributions of the two lifetime components, τ_1 and τ_2, in the bi-exponential analysis of the decays.

Concentration of SCX4 (mM)	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
0	-	-	1.4	100
1.8	1.0	14	1.4	86
3.8	1.1	45	1.4	55
6.0	1.1	46	1.4	54
8.8	1.1	54	1.4	46
13.5	1.1	70	1.4	30
17.9	1.1	79	1.4	21
22.7	1.1	88	1.4	12

[a] The fluorescence decays are fitted by considering either single or bi-exponential functions; with general expression as, $I(t) = \sum_i a_i \exp(t / \tau_i)$ .The relative contribution of each decay component τ_i, is calculated as, $A_i = a_i \tau_i / \sum_i a_i \tau_i$. 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, τ_1 and τ_2, in the bi-exponential analysis of the decays.

Concentration of SCX6 (mM)	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
0	-	-	1.4	100
0.45	0.65	3	1.4	97
3.5	0.63	7	1.4	93
5.9	0.58	10	1.4	90
7.9	0.60	12	1.4	88
10.5	0.60	16	1.4	84
13.0	0.57	17	1.4	83
16.1	0.56	20	1.4	80
19.1	0.55	23	1.4	77
22.5	0.55	26	1.4	74

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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:

$$\tau_{free} = \frac{1}{k_f + k_{nr}} \tag{1}$$

$$\tau_{bound} = \frac{1}{k'_f + k'_{nr} + k_q} \tag{2}$$

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 (τ_f) is 2.1 ns, radiative rate constant (k_f) is 5.2×10^7 s^{-1} and the nonradiative rate constant (k_{nr}) is 4.2×10^8 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 6.6×10^8 s^{-1}.

Since QZ binds very loosely to the wide SCX6 cavity, it is quite reasonable to assume that for the SCX6-QZ system, $k_f \approx k'_f$ 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 9.6×10^8 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 6.4×10^8 s^{-1} (i.e. $[4/6]\times9.6\times10^8$ 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 S_1) and the calculated k_q value (6.4×10^8 s^{-1}), one can have the following relation to be justified for the SCX4-QZ system,

$$k'_{f(SCX4\bullet QZ)} + k'_{nr(SCX4\bullet QZ)} = (\tau^{-1}_{SCX4\bullet QZ} - k_q) = 2.6\times10^8 s^{-1} \tag{3}$$

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

$$\frac{\phi_{SCX4\bullet QZ}}{\phi_{QZ}} = \frac{k'_{f(SCX4\bullet QZ)}\tau_{SCX4\bullet QZ}}{k_{f(QZ)}\tau_{QZ}} \tag{4}$$

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, τ_{QZ} and $\tau_{SCX4\bullet QZ}$, the $k'_{f(SCX4\bullet QZ)}$ value is calculated to be 13.5×10^7 s^{-1}, which is much higher than the $k_{f(QZ)}$ value of 5.2×10^7 s^{-1} for free QZ.

Accordingly, $k'_{nr(SCX4\bullet QZ)} = 1.3\times10^8$ s^{-1} and $\Delta k_{nr} = (k'_{nr} - k_{nr}) = -5.2\times10^8$ 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,

$$\mathrm{SCXn} + \mathrm{QZ} \xrightleftharpoons{K_{eq}} \mathrm{SCXn} \bullet \mathrm{QZ} \tag{6}$$

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

$$K_{eq} = \frac{[\mathrm{SCXn} \bullet \mathrm{QZ}]}{[\mathrm{QZ}][\mathrm{SCXn}]} = \frac{[\mathrm{SCXn} \bullet \mathrm{QZ}]}{\{[\mathrm{QZ}]_0 - [\mathrm{SCXn} \bullet \mathrm{QZ}]\}\{[\mathrm{SCXn}]_0 - [\mathrm{SCXn} \bullet \mathrm{QZ}]\}} \approx \frac{[\mathrm{SCXn} \bullet \mathrm{QZ}]}{\{[\mathrm{QZ}]_0 - [\mathrm{SCXn} \bullet \mathrm{QZ}]\}[\mathrm{SCXn}]_0} \tag{7}$$

or, $$[\mathrm{SCXn} \bullet \mathrm{QZ}] = K_{eq}[\mathrm{QZ}]_0[\mathrm{SCXn}]_0 - K_{eq}[\mathrm{SCXn} \bullet \mathrm{QZ}][\mathrm{SCXn}]_0 \tag{8}$$

or, $$\{1 + K_{eq}[\mathrm{SCXn}]_0\}[\mathrm{SCXn} \bullet \mathrm{QZ}] = K_{eq}[\mathrm{QZ}]_0[\mathrm{SCXn}]_0 \tag{9}$$

or, $$\frac{[\mathrm{SCXn} \bullet \mathrm{QZ}]}{[\mathrm{QZ}]_0} = \frac{K_{eq}[\mathrm{SCXn}]_0}{1 + K_{eq}[\mathrm{SCXn}]_0} \tag{10}$$

and $$\frac{[\mathrm{QZ}]}{[\mathrm{QZ}]_0} = 1 - \frac{[\mathrm{SCXn} \bullet \mathrm{QZ}]}{[\mathrm{QZ}]_0} = 1 - \frac{K_{eq}[\mathrm{SCXn}]_0}{\{1 + K_{eq}[\mathrm{SCXn}]_0\}} = \frac{1}{\{1 + K_{eq}[\mathrm{SCXn}]_0\}} \tag{11}$$

Further, if it is considered that C_{QZ} and $C_{SCXn \bullet QZ}$ are the relative percentage contributions of QZ and $\mathrm{SCXn} \bullet \mathrm{QZ}$ in the observed fluorescence decay, then we have,

$$C_{QZ} + C_{SCXn \bullet QZ} = 100 \tag{12}$$

It is understandable that the individual contributions C_{QZ} and $C_{SCXn \bullet QZ}$ will be proportional to their respective relative populations. Hence we can write,

$$C_{QZ} = k_{QZ} \frac{[QZ]}{[QZ]_0} \tag{13}$$

and $$C_{SCXn\bullet QZ} = k_{SCXn\bullet QZ} \frac{[SCXn \bullet QZ]}{[QZ]_0} \tag{14}$$

where k_{QZ} and $k_{SCXn\bullet QZ}$ 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,

$$C_{SCXn\bullet QZ} = \frac{k_{SCXn\bullet QZ} K_{eq}[SCXn]_0}{\{1 + K_{eq}[SCXn]_0\}} \tag{15}$$

and $$C_{QZ} = \frac{k_{QZ}}{\{1 + K_{eq}[SCXn]_0\}} \tag{16}$$

References

1. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, 2006.

2. D. K. Palit, H. Pal, T. Mukherjee and J. P. Mittal, *J. Chem. Soc. Faraday Trans.*, 1991, **86**, 3861.