

Table SI 1. Adsorption data from ethanol and buffered ethanol of dyes onto nanocrystalline TiO₂. The binding constants and maximum coverage values were determined using a global Langmuir analysis of all dyes within one solvent system, or by an individual analysis using a Henry's law approach and the coverage found from the Langmuir analysis.

Ethanol			Ethanol/py/pyH ⁺		
Langmuir			Langmuir		
mol _{ads} ^{max} =			mol _{ads} ^{max} =		
Henry			Henry		
100±10 nmol			60±5 nmol		
cm ⁻²			cm ⁻²		
<i>K</i> _{ads}		<i>K</i> _{ads}	<i>K</i> _{ads}		<i>K</i> _{ads}
(μM ⁻¹)		(μM ⁻¹)	(μM ⁻¹)		(μM ⁻¹)
[Ru(L'')L ₂] ⁺	0.006±0.001	0.008±0.0004	[Ru(HL'')L ₂] ²⁺	0.06±0.02	0.03±0.006
[Ru(L')L ₂] ⁰	0.06±0.01	0.05±0.007	[Ru(H ₂ L')L ₂] ²⁺	0.3±0.1	0.1±0.04
[Ru(HL') ₂ (H ₂ L')] ⁰	0.3±0.07	0.2±0.02	[Ru(H ₂ L') ₃] ²⁺	0.05±0.02	0.1±0.01
[Ru(H ₂ L') ₂ (CN) ₂] ⁰	0.1±0.03	0.06±0.003	[Ru(H ₂ L') ₂ (CN) ₂] ⁰	2±1	0.5±0.09
[Ru(H ₂ L') ₂ (NCS) ₂] ⁰	0.08±0.02	0.05±0.002	[Ru(H ₂ L') ₂ (NCS) ₂] ⁰	16±13	0.4±0.2

a: Global fit to the Langmuir isotherm Eq. 6 with mol_{ads}^{max} as the global parameter.

b: Straight line fit (intercept = 0) to data for low equilibrium concentrations with mol_{ads}^{max} = 104 nmol cm⁻².

c: Straight line fit (intercept = 0) to data for low equilibrium concentrations with mol_{ads}^{max} = 57 nmol cm⁻².

Table SI 2: Nanocrystalline TiO₂ Adsorption Kinetics. The initial dye concentrations are in all cases much greater than the maximum amount of dye that can be adsorbed on the surface. The integration of eq. 3c (with c_{dye} constant) yields: $\theta = A(1 - e^{-k_{\text{ads}}t})$ where $k_{\text{obs}} =$

$$k_{\text{ads}}c_{\text{dye}} + k_{\text{des}} \text{ and } A = K_{\text{ads}}c_{\text{dye}}/(K_{\text{ads}}c_{\text{dy}}+1).$$

Complex	Solvent	dye conc. (μM)	A (h^{-1})	k_{obs} (h^{-1})	slope ^a ($\text{mM}^{-1} \text{h}^{-1}$)	Intercept ^a $\times 10^2$ (h^{-1})
[Ru(L')L ₂] ⁺	EtOH	20	0.055	0.45		
		55	0.28	0.19	-0.5±2	40±10
		125	0.91	0.35		
[Ru(L')L ₂] ⁰	EtOH	10	0.49	0.046		
		50	0.82	0.32	7.2±0.4	-4±2
		110	0.96	0.72		
[Ru(HL')(H ₂ L')] ⁰	EtOH	10	0.49	0.046		
		50	0.69	0.41	9.5±0.5	-5±1
		110	0.86	0.90		
[Ru(H ₂ L') ₂ (CN) ₂] ⁰	EtOH	10	0.30	0.094		
		50	0.86	0.23	8±1	-4±10
		110	0.99	0.77		
[Ru(H ₂ L') ₂ (NCS) ₂] ⁰	EtOH	10	0.17	0.030		
		60	0.87	0.21	4.6±0.5	-4±3
		110	0.99	0.50		
[Ru(H ₂ L') ₂ (NCS) ₂] ⁰	EtOH/py/pyH ⁺	10	0.63	0.038		
		60	0.82	0.55	11±2	-10±10
		110	0.95	1.33		

a: Slope and intercept from plot of k_{obs} vs dye concentration.