

Supporting Information:

I. Total Internal Reflection set-up in our laboratory

For Total internal reflection Fluorescence measurements the excitation laser beam was vertically polarized and was focused onto the solid/liquid interface with a biconvex lens of focal length 7.5cm. The incident angle ($\theta_i \sim 68^\circ$) of the excitation beam was set at an angle greater than critical angle. For the Total internal reflection (TIRF) experiments circular sample-cell is made from Kel-F polymer, containing a concentric well and four peripheral clamping holes. The sample fills the well. A fused silica hemispherical prism (diameter: 1") is sealed to the top of the sample with an O-ring seal. The cell is vertically mounted facing the detector. A cylindrical lens of focal length 5cm placed between the prism and the detector focuses the resultant fluorescence signal travelling through the prism into the detector. The fluorescence is detected by the PMT tube facing the prism. The emission polarizer is set at magic angle $\sim 54.7^\circ$.

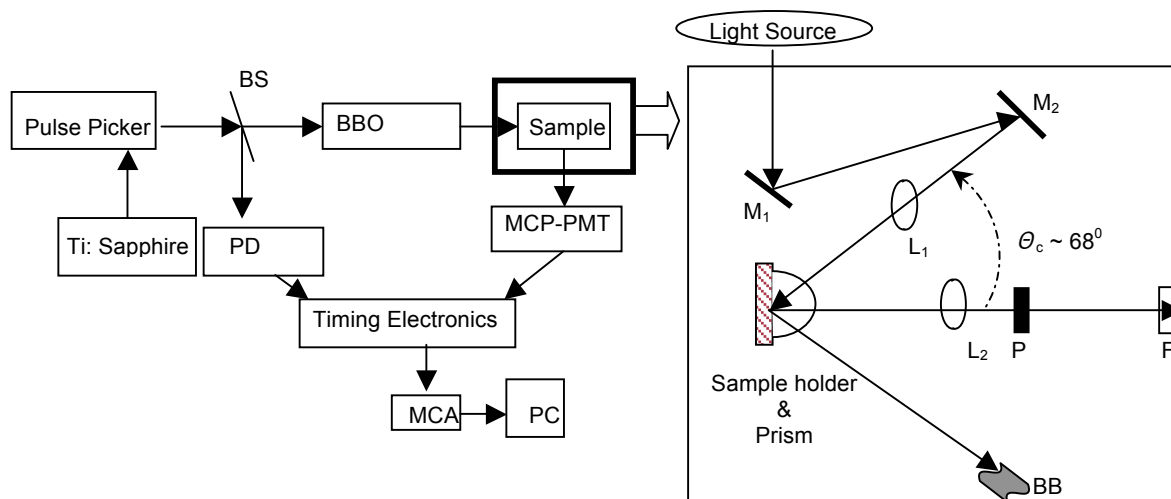


Figure SI-1: Schematic of TCSPC set-up under TIRF mode at solid/liquid interface. Key: BS is the beam splitter. BBO is the β -barium borate crystal (frequency doubler). PD is the photodiode. MCP-PMT is the microchannel photomultiplier tube. MCA is the multi channel card analyzer for data acquisition. M_1 and M_2 are the mirrors. P is for the polarizer. L_1 and L_2 are the biconvex and cylindrical lenses respectively. F is the filter holder. BB is the beam blocker.

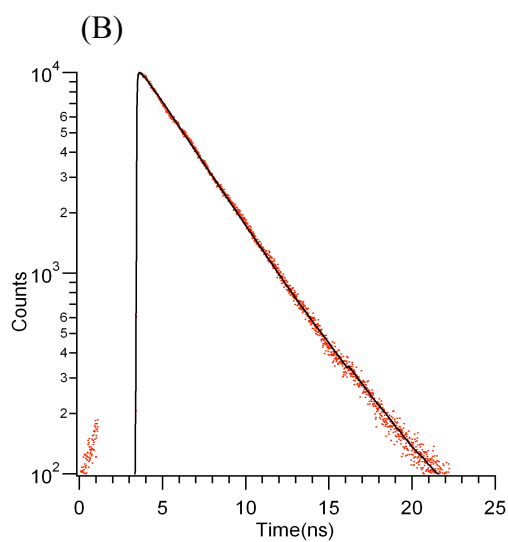
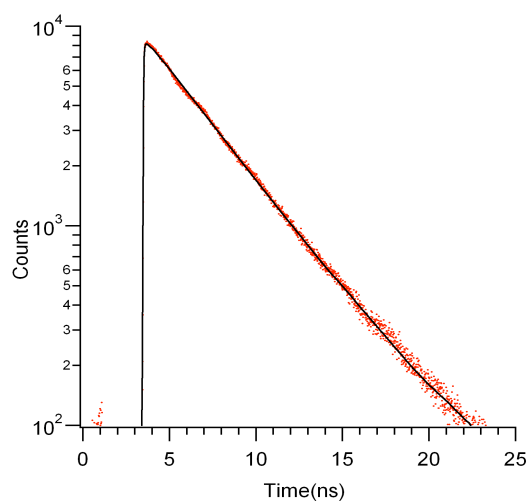


Figure SI-2: Fluorescence decay curve of (A) C152 in bulk decane, $\tau \sim 4.00$ ns (B) C461 in bulk decane, $\tau \sim 3.45$ ns. The lifetime of C152 in bulk decane is longer than in bulk methanol due to the alkane's inability to stabilize a TICT state. (Ref: S. Nad, M. Kumbhakar and H. Pal, *J. Phys. Chem. A.*, 2003, **107**, 4808-4816). The lifetime of C461 in bulk methanol is 3.22 ns and is comparable to the bulk decane result implying that solvent polarity does not stabilize preferentially new conformers of this solute.

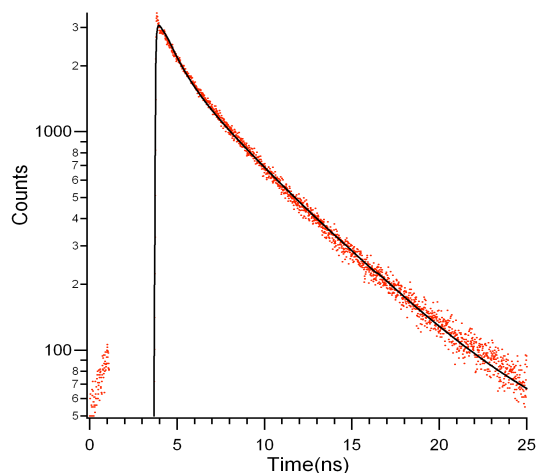


Figure SI-3: Fluorescence decay curve of C152 at silica/vapor interface. This film was formed from a methanol solution having a bulk concentration of 0.5mM. The data trace fit very well to a double exponential decay with the longer and shorter lifetimes similar to those measured at the silica/methanol interface. The longer lifetime is assigned to solutes in direct contact with the silica surface and the shorter lifetime is assigned to solutes in the multilayer. At the silica/vapor interface the signal from the adsorbed solutes gets enhanced as compared to silica/methanol signal.

SI- Table I.

Filters	A_1	τ_1 (ns)	A_2	τ_2 (ns)	χ^2
420 LPF	0.60	5.00	0.40	0.98	1.5