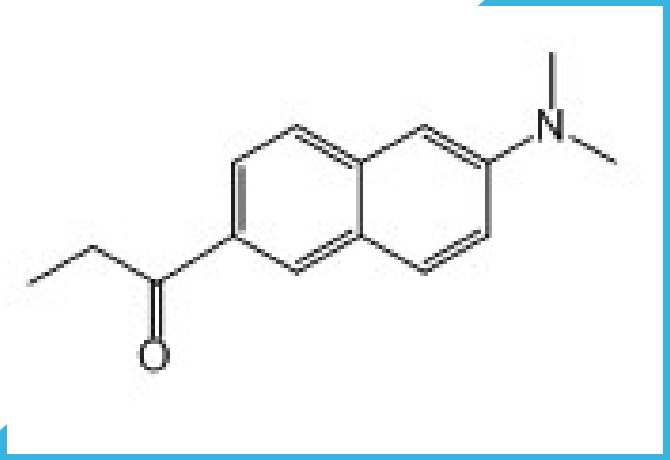
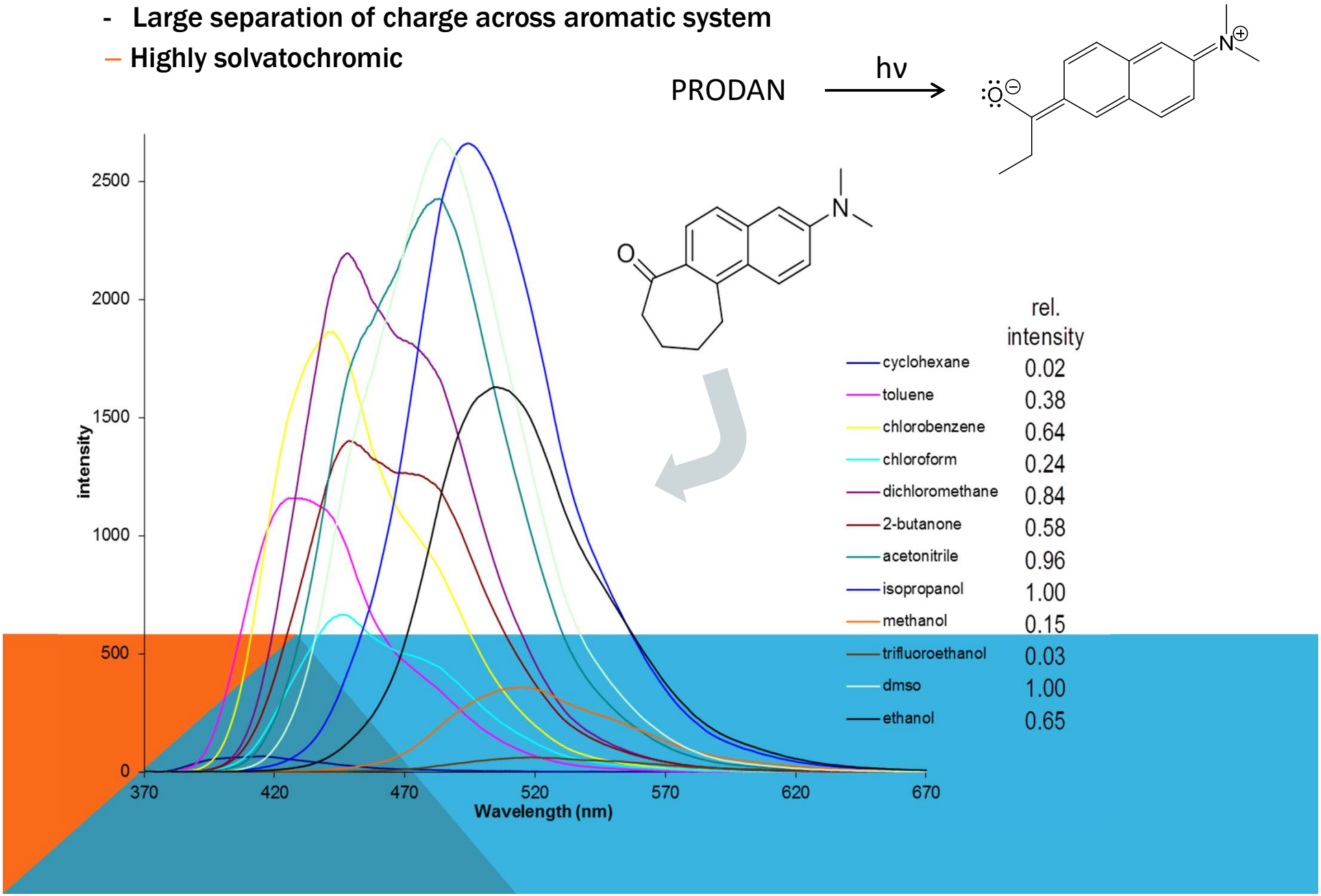
FLUOESCENT CHEMOSENSORS OF MICROACIDITY AND DIPOLARITY: STRUCTURE AND FUNCTION



6-propionyl-2-dimethylaminonaphthalene (PRODAN)

- **PRODAN was synthesized 1979 as fluorescent probe of bovine serum albumin**
  - Large separation of charge across aromatic system
  - Highly solvatochromic

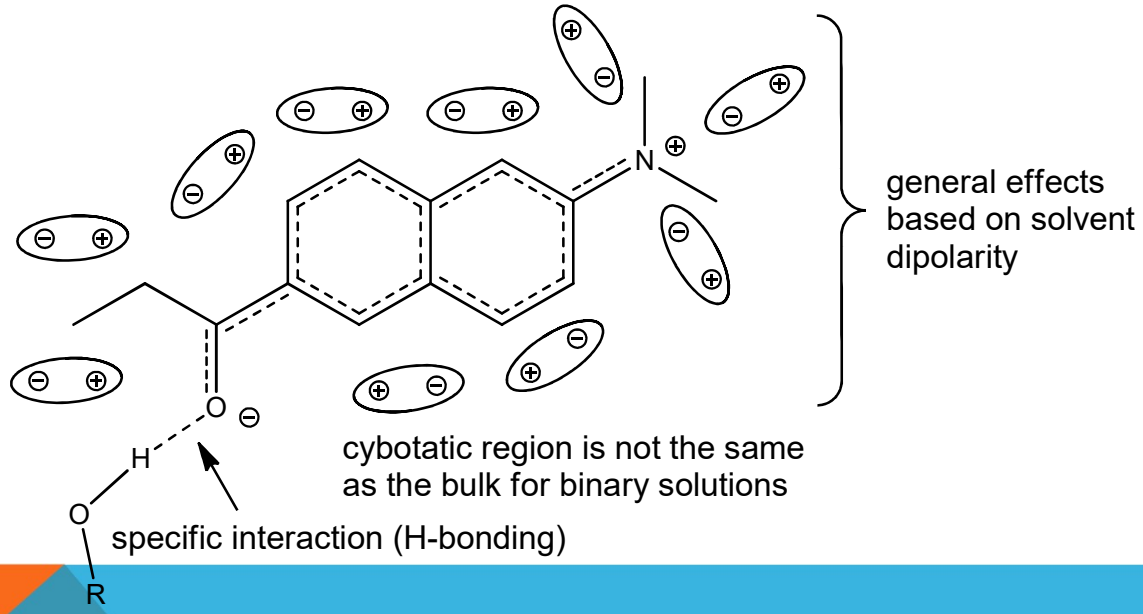


SOLVENT EFFECTS

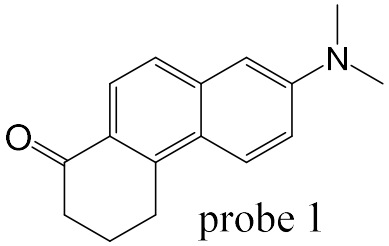
A solvent can be characterized by its acidity (SA), basicity (SB), polarizability (SP), and dipolarity (SdP)

With PRODAN

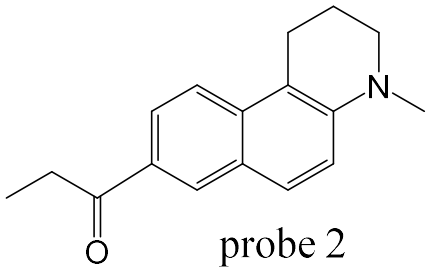
- **H-bond donating solvents (high SA) lead to a little fluorescence quenching**
- **Polar solvents (high SdP) leads to red-shifted emission (solvatochromism)**



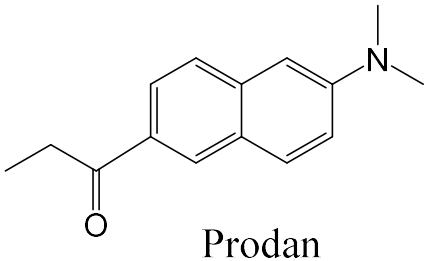
EARLY WORK:



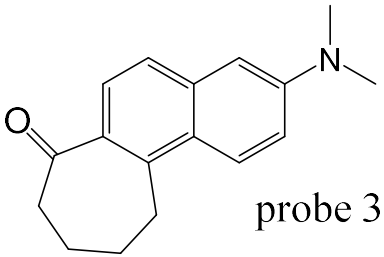
probe 1



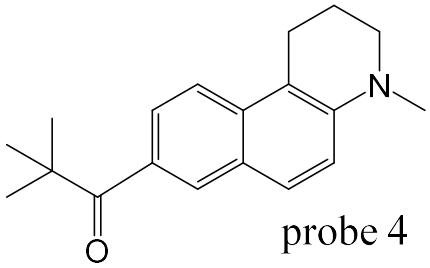
probe 2



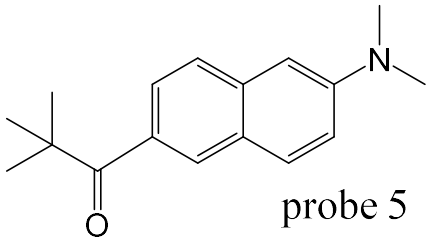
Prodan



probe 3



probe 4



probe 5

Forced planar at carbonyl (1)
or amine (2)

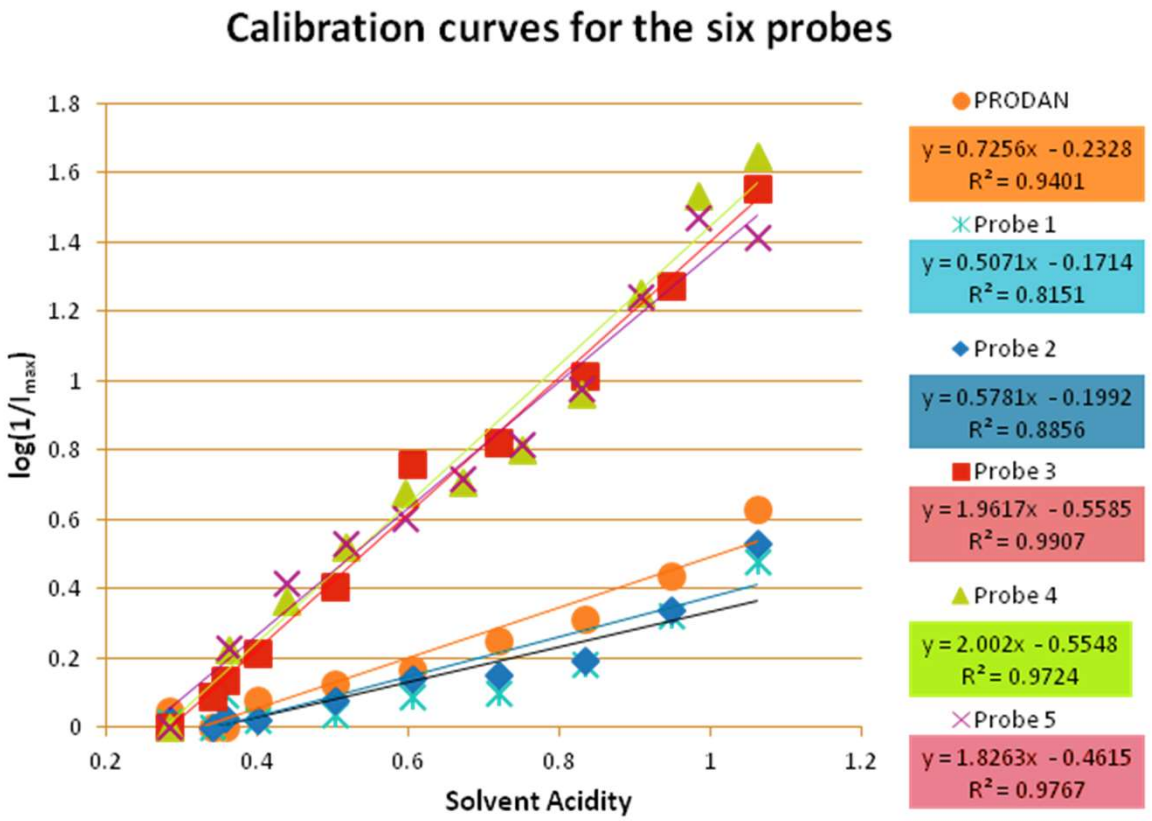
Forced to twist at carbonyl

PRODAN emits from a planar intramolecular charge-transfer (PICT) excited state

probes 1 & 3 - Everett, Nguyen, Abelt *J. Phys. Chem. A* **2010**, *114*, 4946–4950.
probes 2 & 4 - Lobo , Abelt *J. Phys. Chem. A*, **2003,** *107* , 10938-10943.
probe 5 - Green, Naughton, Nealy, Pike, Abelt *J. Org. Chem.*, **2013**, *78,* 1784–1789

CHEMOSENSORS OF SOLVENT ACIDITY

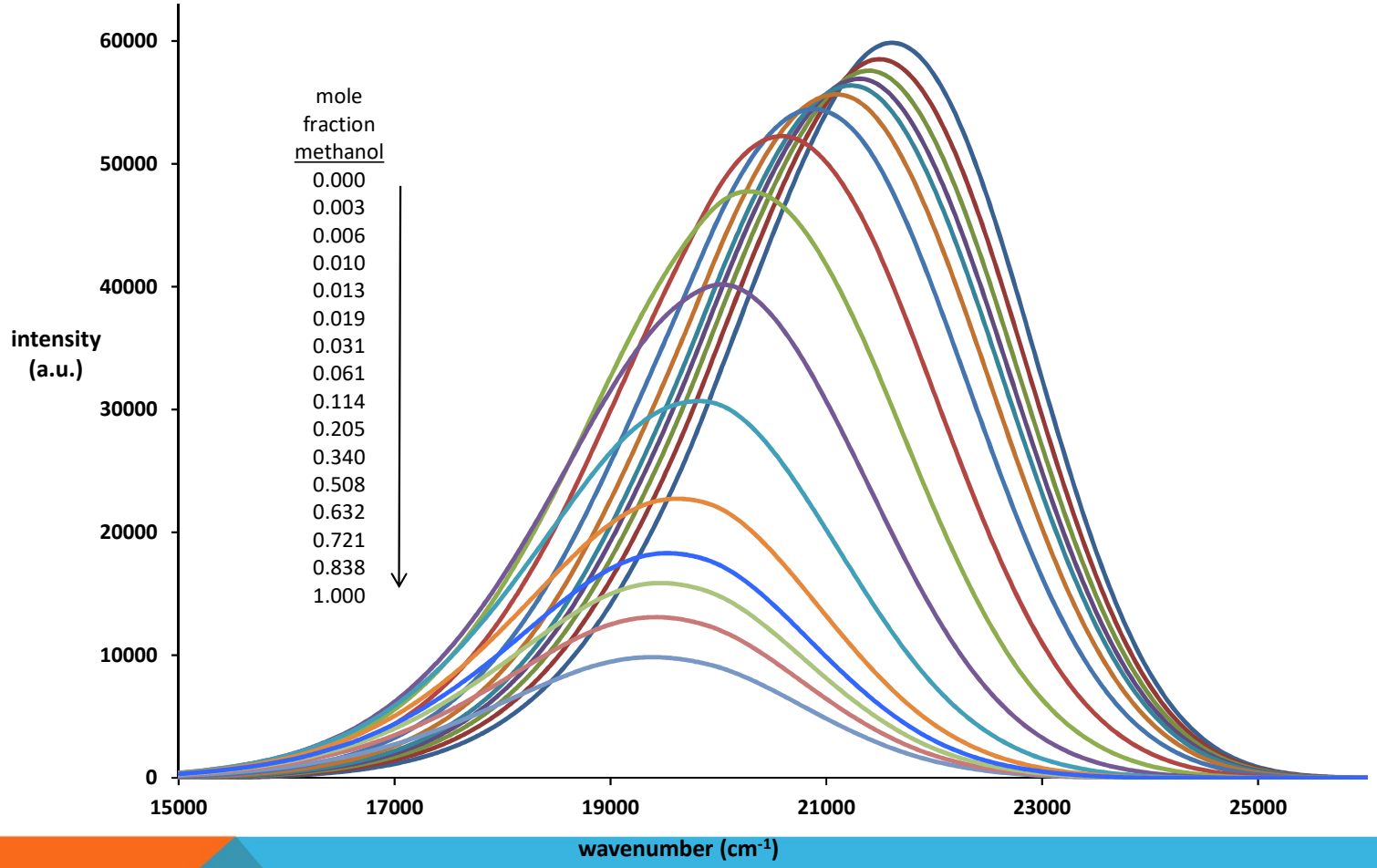
Solvents	Solvent Acidities
Isopropanol	0.283
Water	1.062
Methanol	0.605
Ethanol	0.400
Propanol	0.367
Butanol	0.341
1,2-propanediol	0.475
ethylene glycol	0.717



Carbonyl-twisted PRODAN derivatives are strongly quenched in protic solvents. They can be used as sensors of microacidity.

Green, Naughton, Nealy, Pike, Abelt *J. Org. Chem.*, **2013**, *78,* 1784–1789

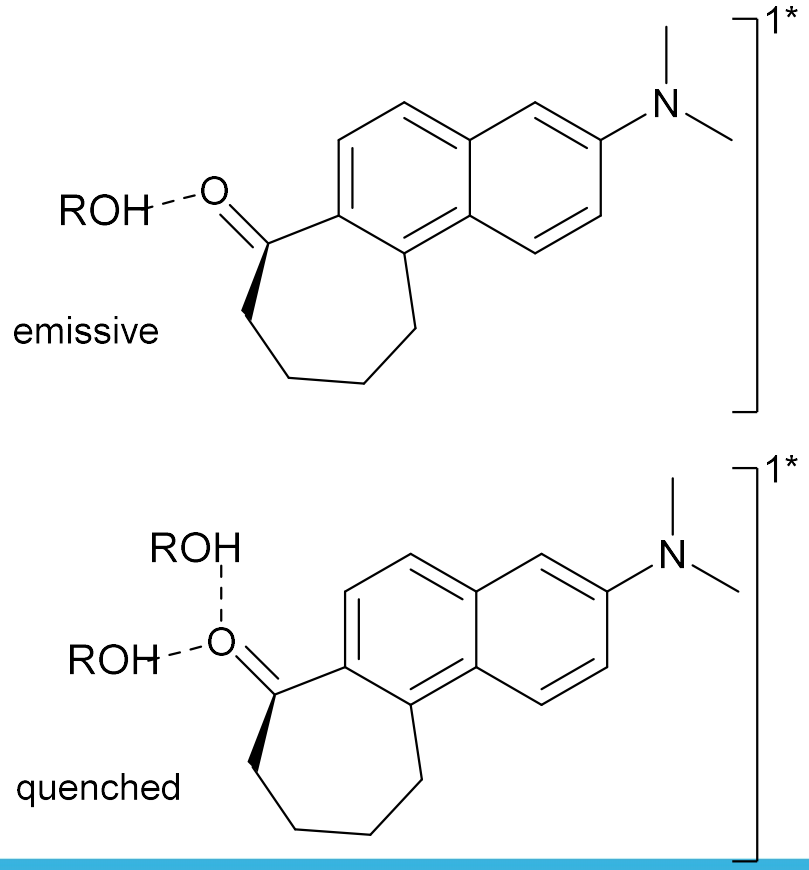
PREFERENTIAL SOLVATION



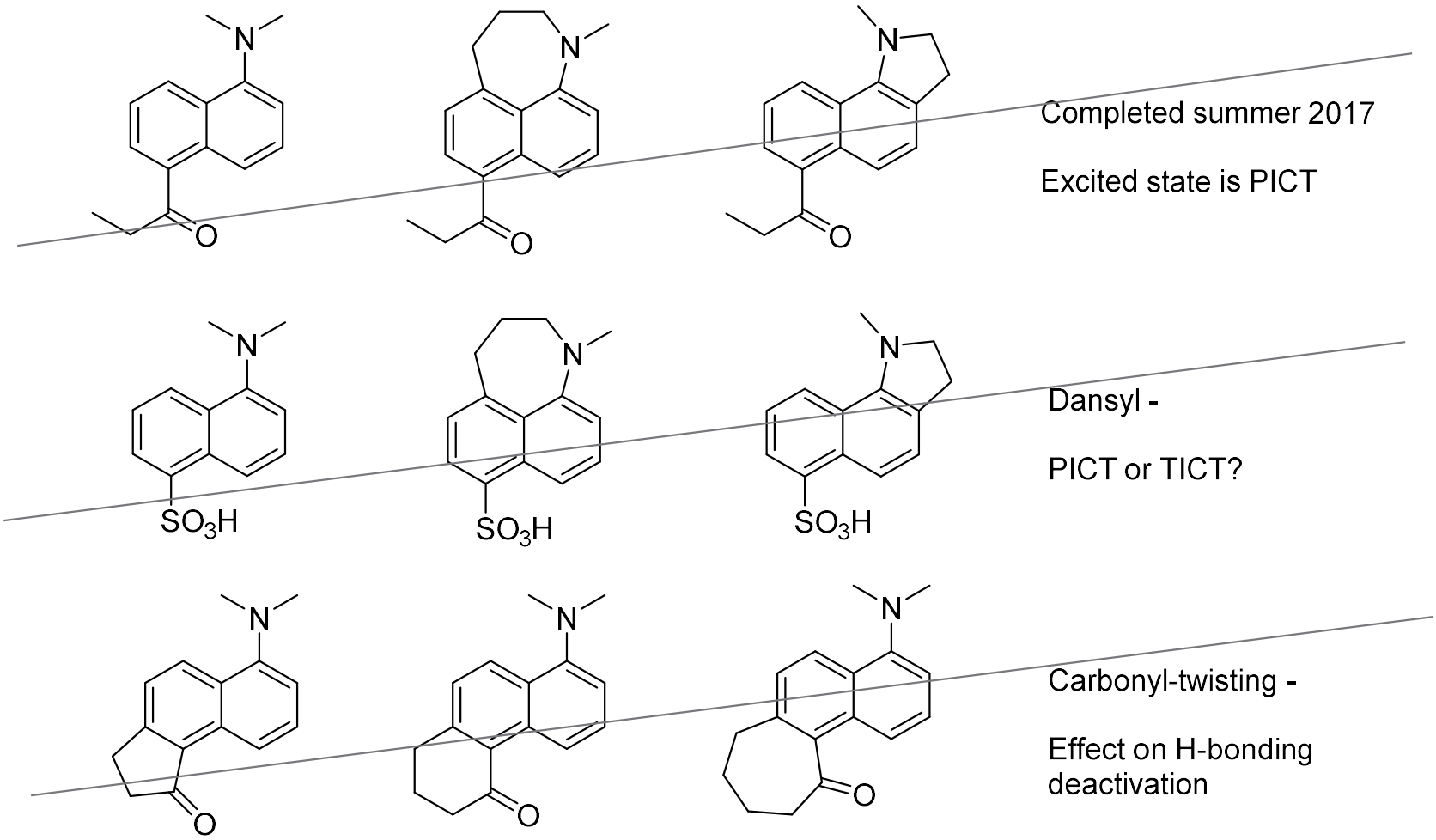
Fluorescence spectra of 4 µM solutions of probe 3 in acetonitrile/methanol mixtures.

Nikitina, Iqbal, Yoon, Abelt *J. Phys. Chem. A* **2013** , *117*, 9189-9195

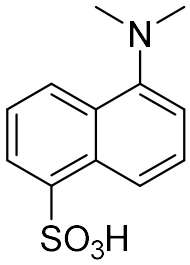
H-BONDING AND QUENCHING

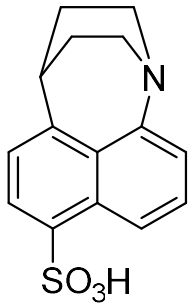


The singly H-bonded excited state is hardly quenched, but its emission shifts significantly. The doubly H-bonded excited state is strongly quenched, but its emission is not much different than that of the singly H-bonded excited state.



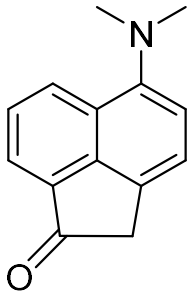
Synthetic targets:
The middle set will be published in 2021

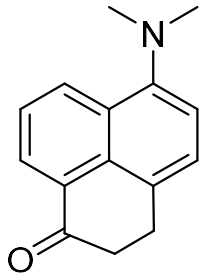


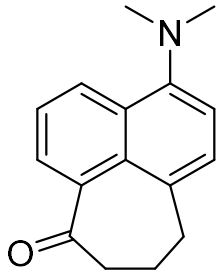


Dansyl -

PICT or TICT?







Carbonyl-twisting and dipole orientation

Effect on H-bonding deactivation

Synthetic targets: