# Ultrafast Processes in Chemistry
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**Module No # 09**
**Lecture No # 47 Part -2**
## Twisted Intramolecular Charge Transfer

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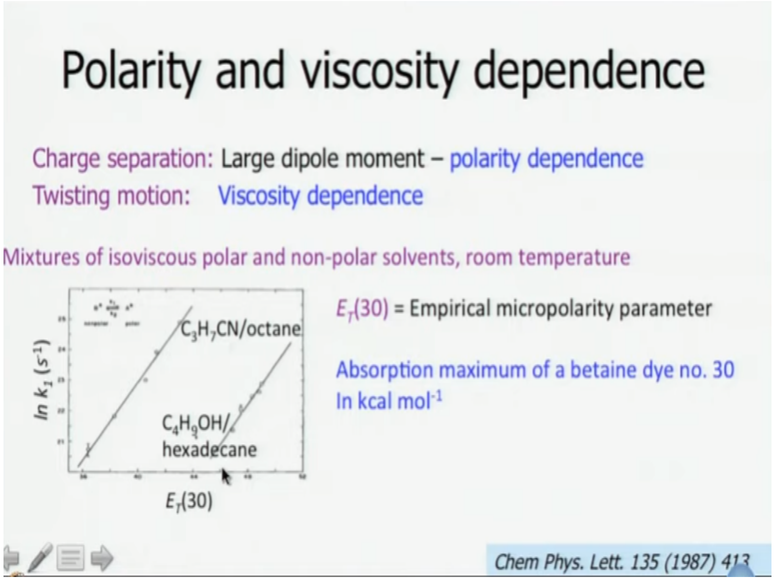

Polarity and viscosity dependence

Charge separation: Large dipole moment – polarity dependence
Twisting motion: Viscosity dependence

Mixtures of isoviscous polar and non-polar solvents, room temperature

$E_T(30)$ = Empirical micropolarity parameter

Absorption maximum of a betaine dye no. 30
In kcal $mol^{-1}$

Chem Phys. Lett. 135 (1987) 413

Okay so we have polarity dependent rate constant that is for sure and there is some effect of hydrogen bonding.

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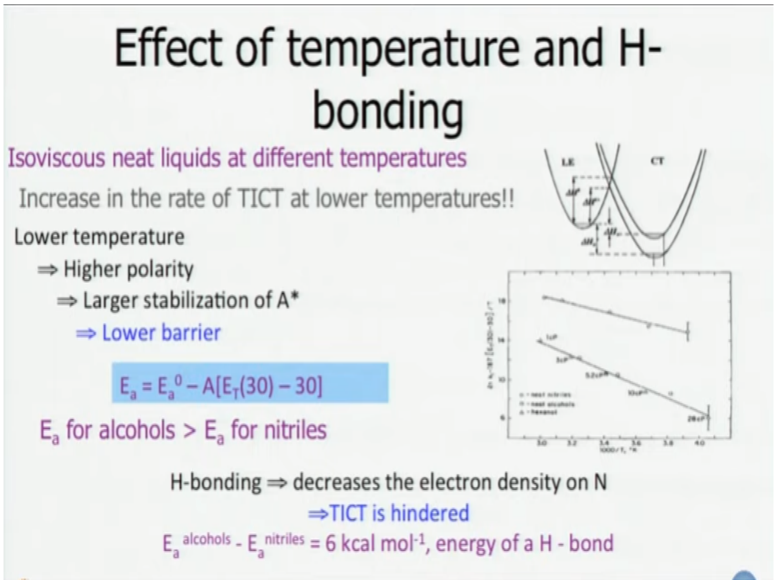

Effect of temperature and H-bonding

Isoviscous neat liquids at different temperatures

Increase in the rate of TICT at lower temperatures!!

Lower temperature
⇒ Higher polarity
⇒ Larger stabilization of A*
⇒ Lower barrier

$E_a = E_a^0 - A[E_T(30) - 30]$

$E_a$ for alcohols > $E_a$ for nitriles

H-bonding ⇒ decreases the electron density on N
⇒TICT is hindered
$E_a^{alcohols} - E_a^{nitriles}$ = 6 kcal $mol^{-1}$, energy of a H - bond

So the second piece of experiment that they did earlier one remember what it was? It was mixtures Isoviscous mixtures at room temperature second experiment in Isoviscous liquid with different temperatures it is important to understand what we are talking about here. As you change the temperature I think it is very well now understood that viscosity of a liquid is going to change does it increase or decrease usually when I increase temperature and what about a gas why?

For a gas viscosity increases with increase in temperature that is right for a light it decreases now molecule collision that is liquid you understand nicely right. What about gases? So you think of laminar flow there is exchange between different Lamili that is why but right now we are talking about liquids anyway. So what we did was they painstakingly determined the viscosities of neat liquids at different temperature and then of course you have to eliminate the you cannot compare an alcohol with non polar solvent okay.

And then at different temperatures they took different solvents keeping in mind that viscosity has to be same for all this points although solvent A at 25 degree centigrade solvent B at 35 degree centigrade solvent C at 45 degree centigrade so on and hence so forth the common known factor is that at 25 degree centigrade whatever viscosity solvent they had is the viscosity of solvent C at 45 degree centigrade okay.

Isoviscous neet liquids in different temperatures and then they observe surprising result that the rate of TICT increases at lower temperature that is not a very usual phenomenon right. It is not as if it is even it is unknown again if you go back to active physical chemistry book but any standard physical chemistry book you will see that the if there is a pre-equilibrium then you are going to have when certain conditions are met you can have a decrease in the rate constant with increase in temperature okay.

But here the explanation is this here let us say is your energy surface for the locally excited state this is the energy surface for the charge transfers state. So what they said is that charge transfer state is going to be stabilize further if polarity is more and polarity is more at low temperature yes so what will happen? You can see there are 2 surfaces here for CT the upper one and the lower one if suppose there are 2 temperatures which one will corresponds to the lower temperature which one will corresponds to higher temperature?

Lower one corresponds to higher temperature or lower temperature actually because at lower temperature your polarity is more or less I did not even discuss that we only talked about viscosity sorry. At lower temperate actually polarity is more is that higher temperature what would happen is your solvent dipole should rotate and all that would cause a decrease in dielectric constant.

So at lower temperatures due to greater polarity this would be stabilized you might think that this should have no effect on the activation energy anyway. Because you are stabilizing the product back what does that I have to do with your activation energy actually something is there what is there? Look at this diagram carefully if it comes down what is the activated complex? It is a point at which the 2 potential energy surfaces for LE and CT cut right.

So if the LE surface is where it is and the CT surface is lowered then what will happen is that the 2 surfaces will intersect at a lower energy point okay. That is what will lead to a decrease in activation energy at low temperature okay. So Arrhenius equation is not violated Arrhenius equations is to the expectation that if you increase the temperature rate should increase but that is true only for constant energy activation energy scenario.

Here the activation energy itself becomes smart because it is not temperature that you are changing and this is instructive because you have to remember when you try to understand the photo physics of any molecule that you change some parameter it is not the only thing that is changing it can have the domino effect. So have to be very careful about what you are actually look at you think you are only changing temperature are you effective viscosity? Are you effecting polarity? Are you effecting molecular aggregation or de-aggregation? One needs to think of that.

So now to conclude this story they observe this empirical expression but Ea = Ea0 – A into ET30-30 now it is accidental degeneracy. The second 30 is nothing to do with a first 30 the first 30 is a roll number second 30 is a number that arises out of experiment it is fortous that they are the same or maybe they make sure that may the change the roll number so that this becomes roll number 30 so that both are 30 but these two 30’s are actually not related okay.

So from here what they established is that the activation energy of alcohols it is greater than the activation energy of nitriles. And more interestingly the difference between the activation energies of alcohols and nitriles is 6 calories per mole. Does this number ring a bell? 6 kilo calories per mole what is it? The 6 kilo calories per mole it is the energy of hydrogen bond so this difference in activation energies of alcohols and nitriles is due to hydrogen bond so hydrogen bond also as a roll to play.

And this 1 letter contains so much of information and it is so instructive it is imperative that we all read this well and understand it. There is more to it what I have presented of course it is important that we understand everything please read this paper great. To conclude this story even though we have over short the time a little bit will finish this and may be today we will stop. So TICT in DMABN is the champion molecule of TICT this is what champion is used very comely especially now in the heydays of material science people make devices they make 200 devices and the one that is best for forming is called the champion device.

So there is no harm in learning from their and calling DMABN the champion molecule of TICT but then that is the not the only prominent TICT molecule there are plenty.

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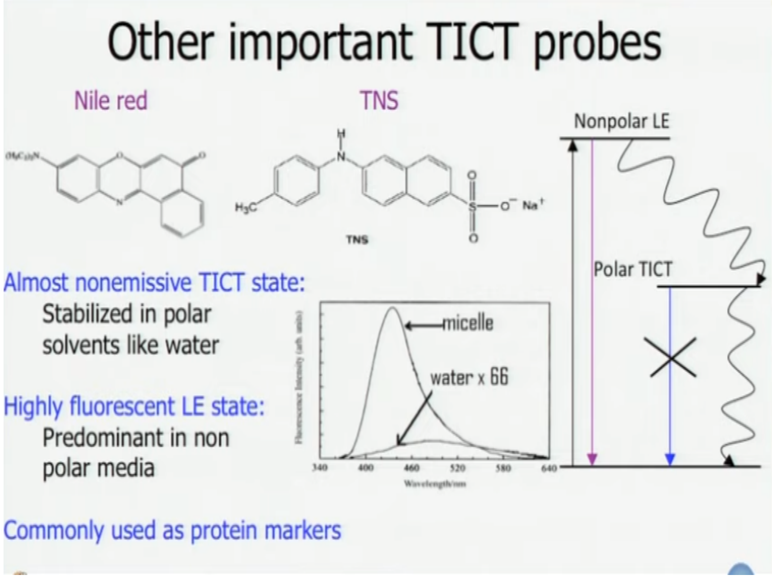

Other important TICT probes

Almost nonemissive TICT state:
Stabilized in polar solvents like water

Highly fluorescent LE state:
Predominant in non polar media

Commonly used as protein markers

2 other these are also champion molecules classes of molecules are Nile red and TNS for ANS for this matter. T for Tolidina A for Aniling so these are all TICT molecules and Nile red and TNS ANS the claim to fame of this molecules is that they are used extensively by people who try to understand proteins using fluorescence. These are very well established protein stains extensive protein stains.

And the idea is and you can see so this is the data that we recorded I think when I was PHD student or something I think this is ANS or TNS I forgot maybe ANS so this is the spectrum in water what multiplied by 66. So if do not multiply by 66 it will be a base line right and you see when we put it in micelle there is a huge increase and there is a blue shift why? This is the TICT emission that you see in water and since TICT state is energetically closer to the ground state non-radiative deactivation of that state is much more that is called the energy gap law.

If the energy gap between 2 states is small then the rate constant of non-radiative deactivation between these 2 states is an exponential function of that energy gap okay widely used in things like metal ion complexes. And when it puts in micelle then the micro polarity is much less that is why the locally excited state is selectively populated that is much , higher energy and more energy okay.

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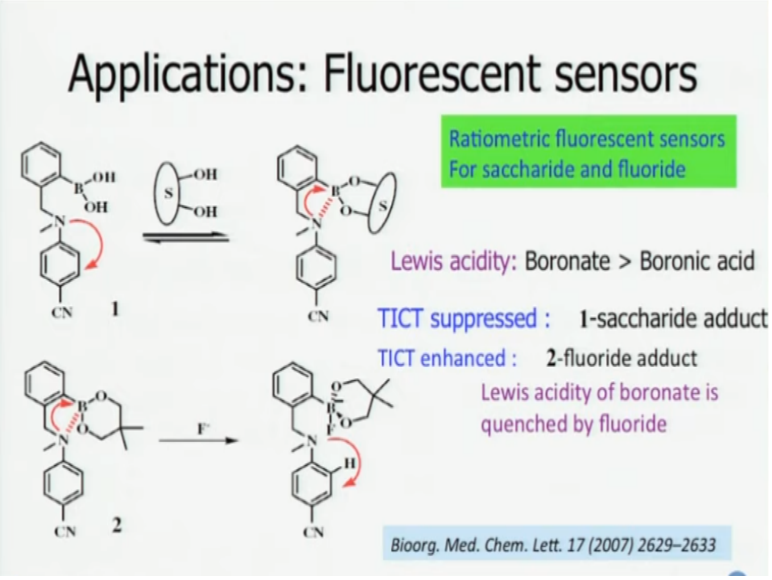

Applications: Fluorescent sensors

Ratiometric fluorescent sensors
For saccharide and fluoride

Lewis acidity: Boronate > Boronic acid

TICT suppressed : 1-saccharide adduct

TICT enhanced : 2-fluoride adduct

Lewis acidity of boronate is
quenched by fluoride

Bioorg. Med. Chem. Lett. 17 (2007) 2629–2633

So this is these are 2 examples and there are many applications that are worked out this is not such a great example I do not know why you have put this one there are if you read the work of say Professor PK Bharadwaj of IIT Kanpur they have made numerous device and all not devices sensors and all and their strategies is always you have an ICT molecule initially ICT is there. Since ICT is there fluorescence is quenched then you bring in a metal ion or whatever you want to sense and that engages the lone pair so ICT is stopped and fluorescence should start that is what makes turn on sensors.

So you can read this is not so bad also you can read this paper for description of this sensor that they made of different thing okay.

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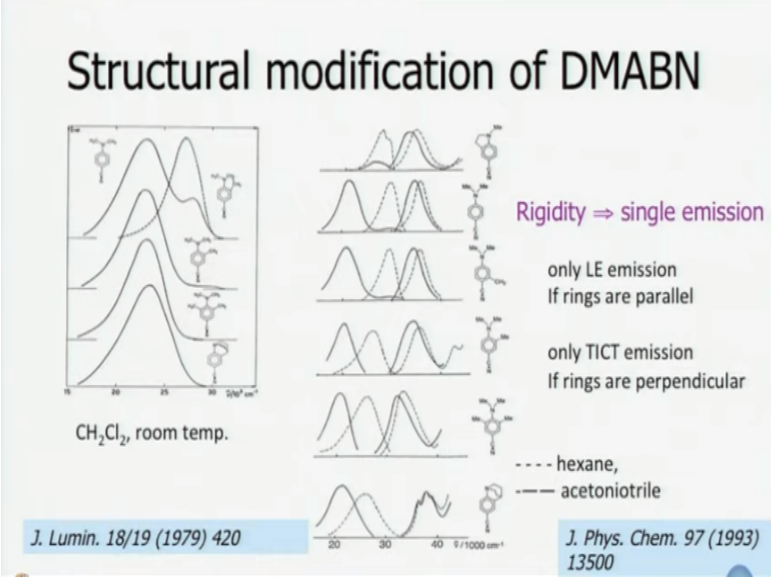

Structural modification of DMABN

$CH_2Cl_2$, room temp.

Rigidity ⇒ single emission

only LE emission
If rings are parallel

only TICT emission
If rings are perpendicular

- - - - hexane,
-—— acetoniotrile

J. Lumin. 18/19 (1979) 420

J. Phys. Chem. 97 (1993) 13500

Now we go back once again to 1993 and show you some data where people where try to do structural modification of DMABN I am going very fast on this part. Because I want you to actually read this papers this is homework I do not expect you to understand everything I am saying right now it is just an introduction. But the crux of the matter is people try to make DMABN derivative of several different structures one in which this co-planarity will be maintained one in which co-planarity is forcibly destroyed.

And in all this studies what they inferred was that the twist takes place if you do not allow the molecule to twist you do not see that TICT band okay. If you force it here 90 degrees you only see the TICT band. But then there are problems also because if you make the linkers a little too long they are results go awry.

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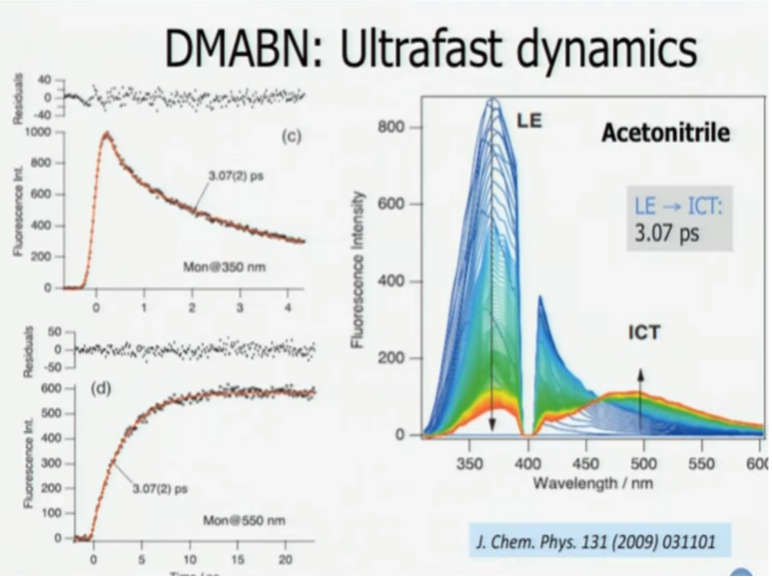
DMABN: Ultrafast dynamics

J. Chem. Phys. 131 (2009) 031101

Now before leaving this subject I should at least show you some real ultrafast dynamics data so let me do that and this is where we will show the data we promised okay. In this 2009 paper what you see is this is what data is this can somebody guess up conversion right but up conversion know the difference as we will see. So this is the dynamics in the blue end of the spectrum okay Mon is not Monday I think it means monitored at 350 nanometer emission wavelength.

You see there is a decay and the decay constants is 3.07 picosecond ignore that 2 in bracket and when this trace is recorded in the red end of the spectrum you get a rise associated with 3.07 picosecond. So this tells that 3.07 picosecond is the time associated with the charge transfer locally excited state to charge transfer state transformation okay. And this is a kind of nice way of putting it. And in case nicer when I show you the time resolved emission spectrum here they are is that something strike you here?

This are not fitting curves these are actual fluorescence spectrum recorded at different time delays the entire fluorescence spectrum is recorded together okay. And now again I want to give another homework is this we are actually gone to our lab and looked at the fox setup and so how it worked femtosecond optical gating depends on generating a sum frequency and as we have discussed earlier for different wave lengths well the gate light is same wave length for different emission wave lengths sum frequency generation would take place at different tilts of the nonlinear crystal and over the last 10 12 modules we have learnt why tilt is important also okay.

So what common sense would tell as is that the tilt at which we get sum frequency for a particular emission wavelength Lambda 1 should not be appropriate to generate sum frequency using another wave length lambda tilt is that right? This is a tilt it is optimum for lambda 1 which means sum frequency well lambda 2 is not going to take place there how do I generate the entire spectrum?

The entire spectrum is recorded at one go like our transient absorption spectrum how has that been done? It can be done in 2 ways first the hard way or the more time consuming way use a stepper motor on sum frequency generation crystal itself right. And keep tilting so this tilt maybe the angle for say emission wave length of what is given here 350 nanometer this maybe the actual the appropriate tilt for 355 nanometer.

So keep on tilting the crystal okay and as you know we use uniaxial crystals so tilt is the only parameter and keep on recording data okay. Hence construct the spectrum but if you want to do that do not forget how it is done fix the tilt then run the scan. So essentially you generate the decay at that wavelength and then change the tilt again record another scan there is a decay. So I this method if you do not want to do in this method you actually generate the decays first and from there you construct the time resolved emission spectrum okay.

The other way of doing it and that is something that we have not really discussed is to use the very thin crystal, in which that tilt is not important. You can get sum frequency for all the wavelengths what I want you do is I want you to read this paper and tell me next day which method has been used in this wavelength. Is it a variable tilt? Or is it a crystal at a particular angle but thin enough so that you can get all the wavelengths together okay.

And in the second case how does it work next day we will start with this question right so we have talked about TICT we have shown plenty of evidences for it and we have discussed the ultrafast dynamics of it we have discussed your applications of it as well. The only thing that remains to be discussed now is the opposition to TICT. Because remember I started off saying that this is perhaps the most controversial excited state process ever discussed maybe not if you get time we will talk about the proton transfer debate between the Tahara and Zewail 7 Aza indol dimers.

And I say Tahara and Zewail because Tahara turned out to be right Zewail turned out to be wrong in that debate that lasted a decade. But why do I say it is controversial TICT. That is because there as been a school of thought minority school of thought which has said from day 1 very vigorously that this twist is not important. And that school has been led by Professor Zachariasse K is the Kiaas. And in heydays of TICT whenever I read their papers I felt that this guy is making too much of sound for no reason.

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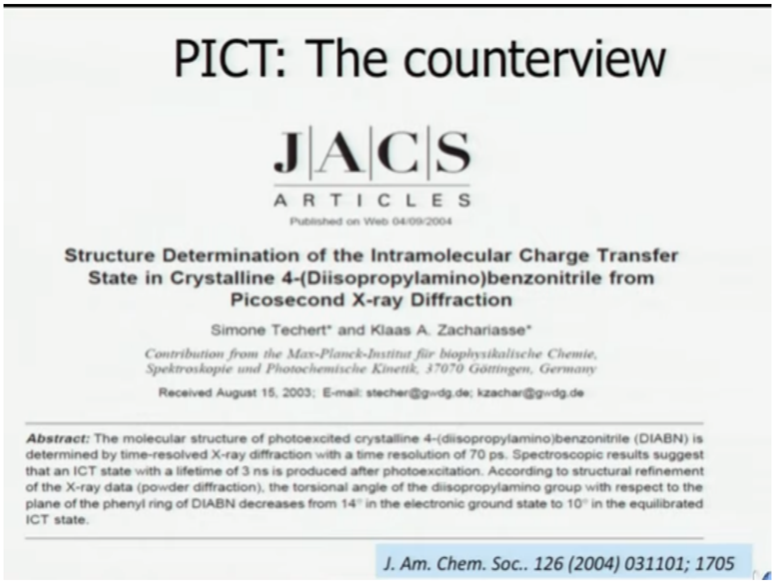

PICT: The counterview

JACS ARTICLES

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**Structure Determination of the Intramolecular Charge Transfer State in Crystalline 4-(Diisopropylamino)benzonitrile from Picosecond X-ray Diffraction**

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***Abstract:*** The molecular structure of photoexcited crystalline 4-(diisopropylamino)benzonitrile (DIABN) is determined by time-resolved X-ray diffraction with a time resolution of 70 ps. Spectroscopic results suggest that an ICT state with a lifetime of 3 ns is produced after photoexcitation. According to structural refinement of the X-ray data (powder diffraction), the torsional angle of the diisopropylamino group with respect to the plane of the phenyl ring of DIABN decreases from 14° in the electronic ground state to 10° in the equilibrated ICT state.

*J. Am. Chem. Soc.. 126 (2004) 031101; 1705*

But then in 2004 or so there was this paper from Zachariasse group and this is a pump probe experiment but it is a UV pump X ray probe experiment and it is easier said that is done it is not so easy to do an X ray probe experiment it is quiet envoy if you read this paper you will see that there are things that we need to do beyond what we have discussed. What is good thing about having an X ray probe who are the people who loved to do X rays? In chemistry department of course inorganic chemist why?

Because they have such strange complicated complexes right so X ray crystallography is what tells them what the structure is and it is not only inorganic chemist even protein crystallographers have to do it okay. So X rays give you the structures so what this paper did is that it showed now you are doing pump probe and probe is x ray so it basically gives you a structure of the molecule in the excited state and when once you know the structure of the molecule in excited state the question of whether it is tilted or whether it is straight in the excited state is laid to rest forever.

Because you can see the structure analysis is not trivial and also the molecule they used it is little different but what they saw there is they said there is an a greater amount of genarization in the excited state compared to the ground state it is completely opposite view TICT says the ground state is planar coplanar excited state is twisted what this guy says is that the ground state is not planar it is something like this excited state is more like this genarization.

So all this discussion falls apart what does not fall apart is the fact that the charge transfer state is highly polar and there is viscosity dependence okay after this paper not many paper have been written on the TICT but it is not as if the debate is over.

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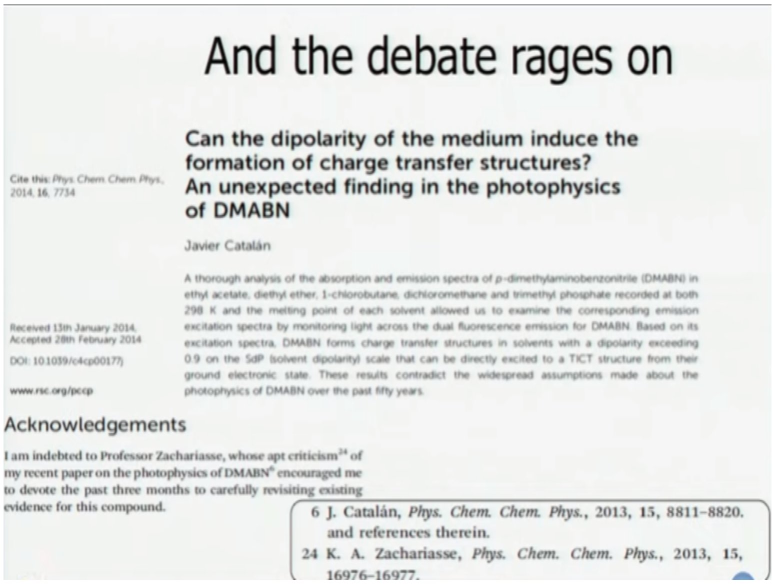

## And the debate rages on

Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 7734

**Can the dipolarity of the medium induce the formation of charge transfer structures? An unexpected finding in the photophysics of DMABN**

Javier Catalán

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www.rsc.org/pccp

A thorough analysis of the absorption and emission spectra of *p*-dimethylaminobenzonitrile (DMABN) in ethyl acetate, diethyl ether, 1-chlorobutane, dichloromethane and trimethyl phosphate recorded at both 298 K and the melting point of each solvent allowed us to examine the corresponding emission excitation spectra by monitoring light across the dual fluorescence emission for DMABN. Based on its excitation spectra, DMABN forms charge transfer structures in solvents with a dipolarity exceeding 0.9 on the SdP (solvent dipolarity) scale that can be directly excited to a TICT structure from their ground electronic state. These results contradict the widespread assumptions made about the photophysics of DMABN over the past fifty years.

**Acknowledgements**

I am indebted to Professor Zachariasse, whose apt criticism[24] of my recent paper on the photophysics of DMABN[6] encouraged me to devote the past three months to carefully revisiting existing evidence for this compound.

6 J. Catalán, *Phys. Chem. Chem. Phys.*, 2013, 15, 8811–8820. and references therein.
24 K. A. Zachariasse, *Phys. Chem. Chem. Phys.*, 2013, 15, 16976–16977.

I leave it you read this paper by Catalan I will only highlight the acknowledgement what you wrote that is that I am indebted to professor Zachariasse whose act criticism of my recent paper on the photo physics of DMABN encourage me to devote the past 3 months to carefully revisiting existing evidence for this compound. So even though the intensity of debate as gone down frequencies of papers as gone down it does not look like anybody is giving up. So over the last the 30 35 years maybe there is intense discussion about what exactly goes on in so called TICT molecules.

One thing is for sure that charged so ICT part of TICT there is no problem whether it is T or whether it is P or whether it is nothing? That is where the debate lies and the useful bi-product if you want to call it that of this debate is that we have first of all got a lot of useful information on this kind of molecules based on which some application have been designed to me what is more important is that in the attempt to understand this the intricacies of this process we have actually learnt a lot about how to perform experiments.

And how to interpret the data if you are going to attempt to answer a question like this to me that is the biggest outcome of this entire debate I will stop here today next day we talk about the thing that is another fundamental that is about another fundamental question how much time does it take for a solvent shell to formed around a polar solute or in other words solvation dynamics.