Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Photophysical Behaviour of 1-(4-N,N-dimethylaminophenylethynyl)pyrene (DMAPEPy) in Homogeneous Media

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Electronic Supplementary Information

1. **^{1}H NMR of DMAPEPy**
2. **^{13}C NMR of DMAPEPy**
3. **High Resolution Mass Spectrum of DMAPEPy**
4. **FTIR Spectrum of DMAPEPy**
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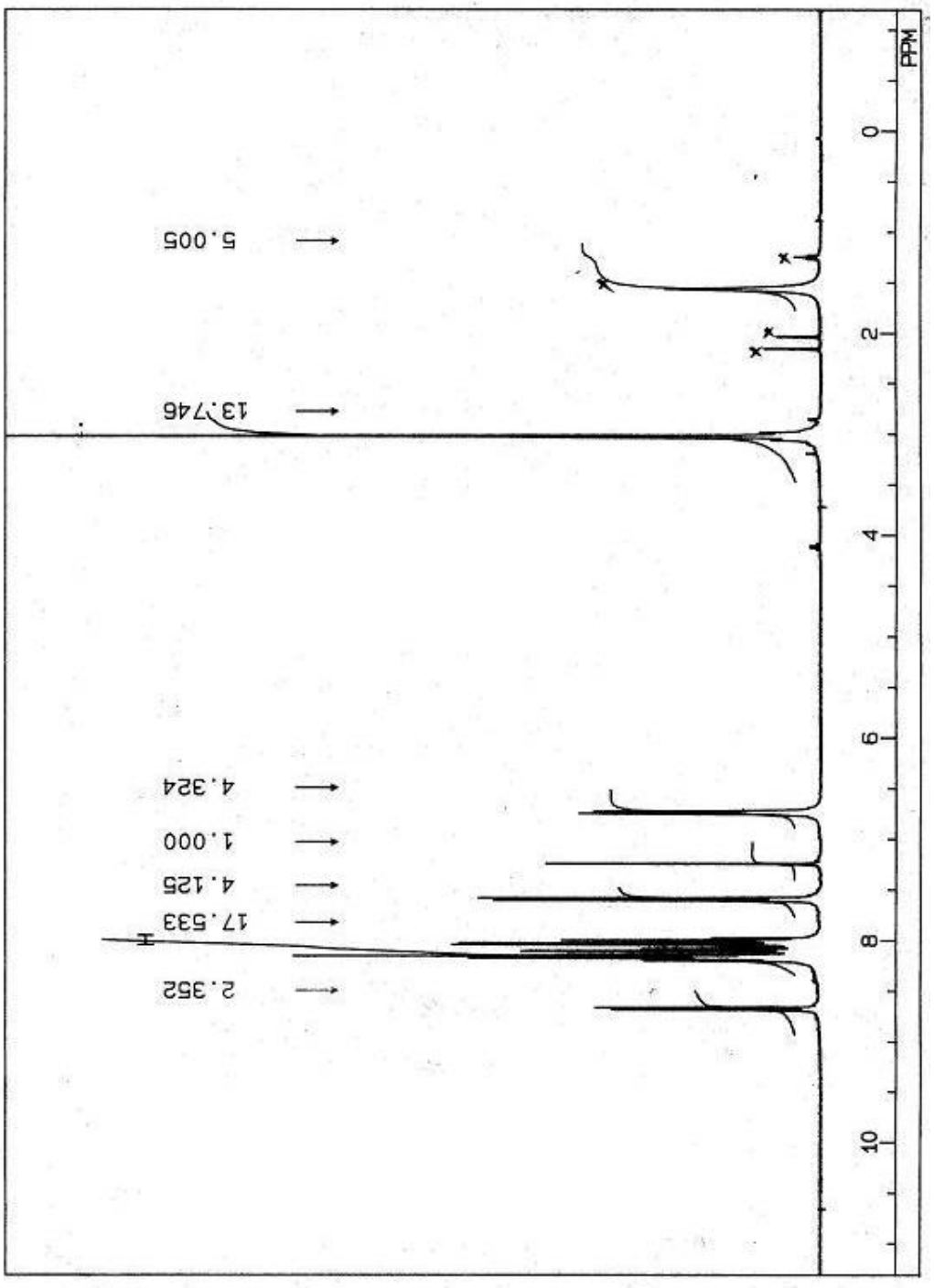
7. **Dependence of k_f on Solvent Polarity**

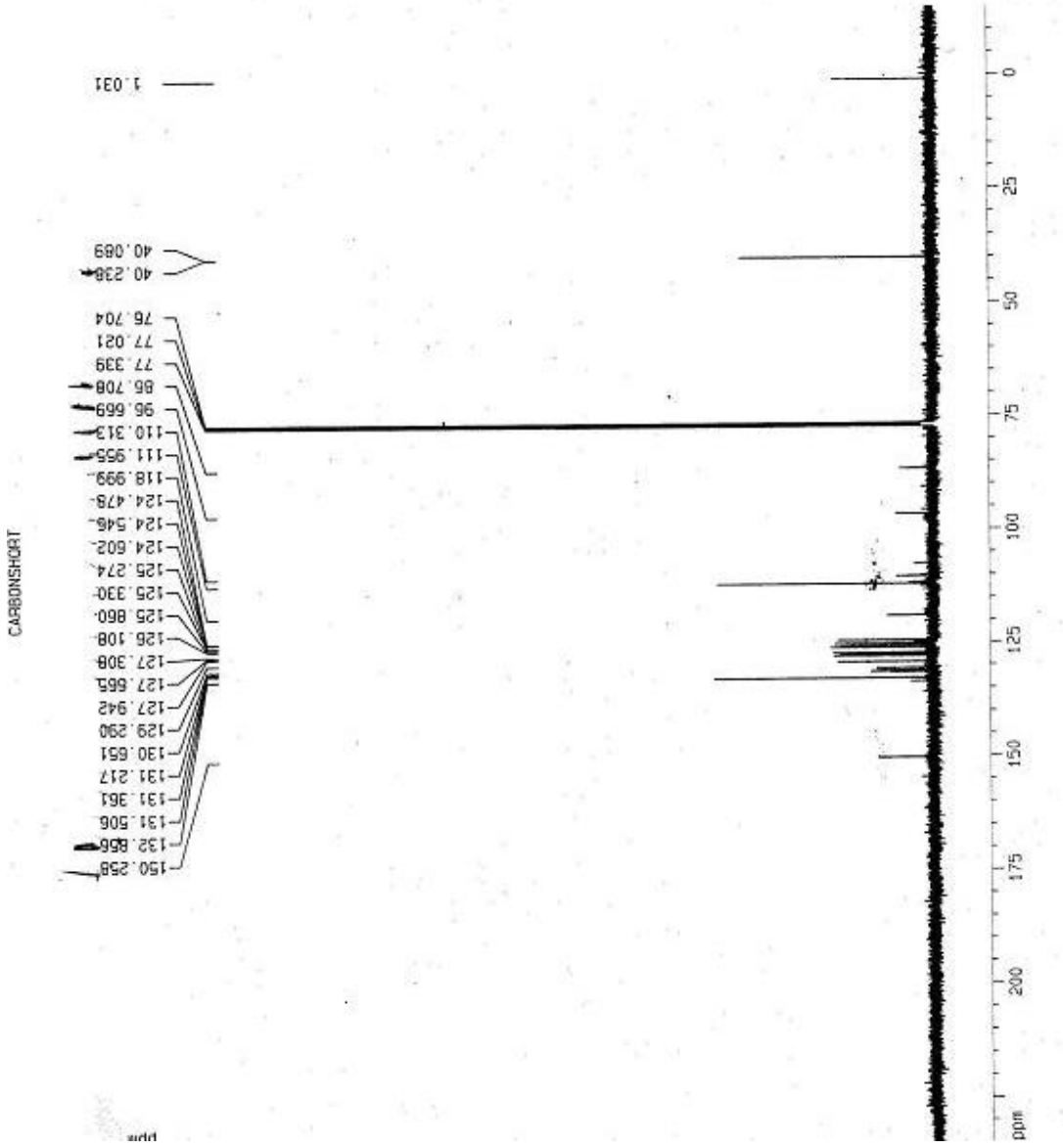
1. ^{1}H NMR Spectrum of DMAPEPy ($CDCl_3$, 400 MHz)

δ = 8.67 (d, J = 8.8 Hz, 1H); 8.17-7.99 (m, 8H); 7.58 (d, J = 8.8 Hz, 2H); 6.73 (d, J = 8.8 Hz, 2H); 2.99 (s, 6H) ppm.



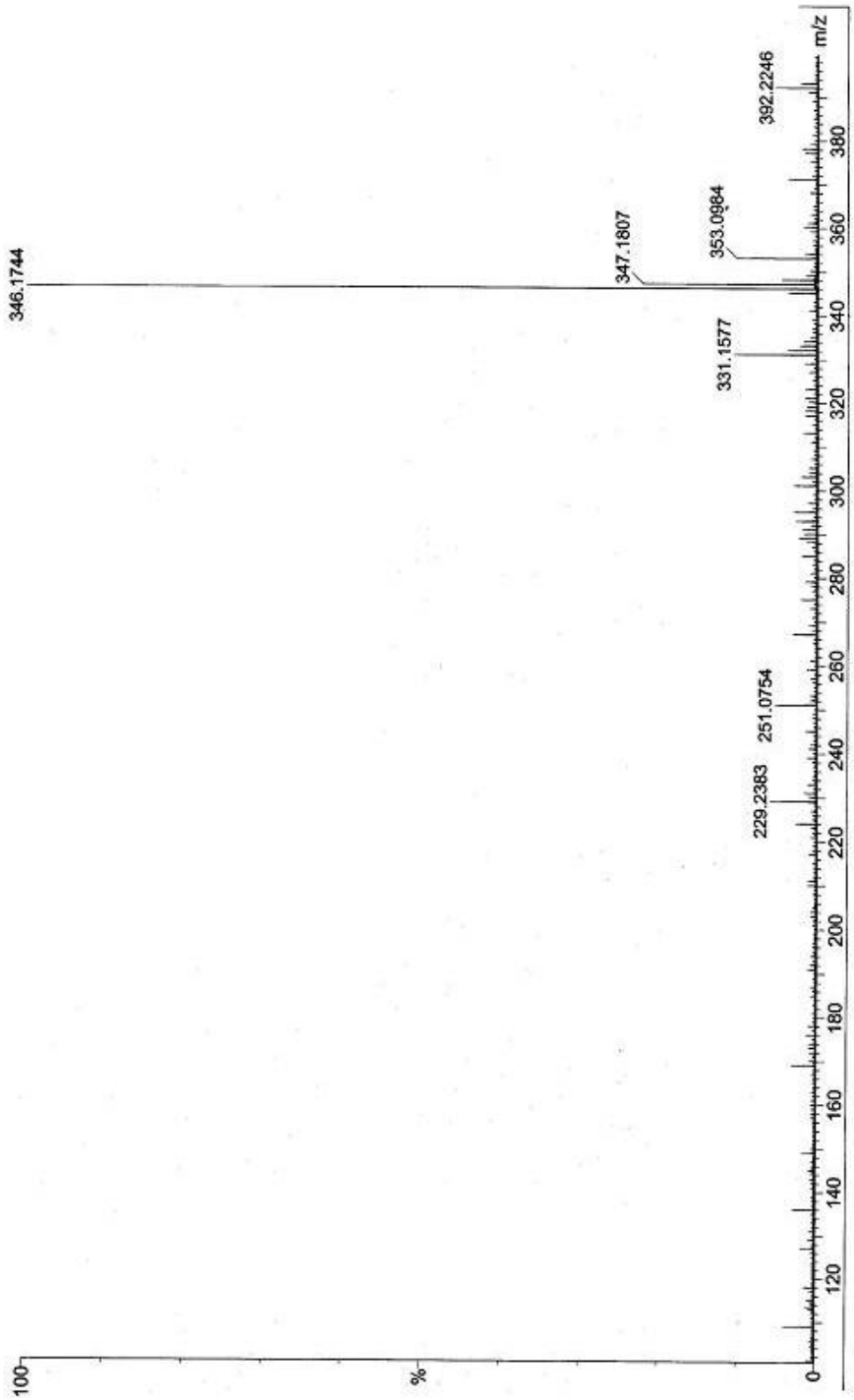
2. ^{13}C NMR Spectrum of DMAPEPy ($CDCl_3$, 100 MHz)

δ = 150.2, 132.8, 131.5, 131.4, 131.2, 130.6, 129.2, 128.0, 127.6, 127.3, 126.1, 125.8, 125.3, 124.5, 124.4, 118.9, 111.9, 110.3, 96.6, 86.7, 40.2 ppm



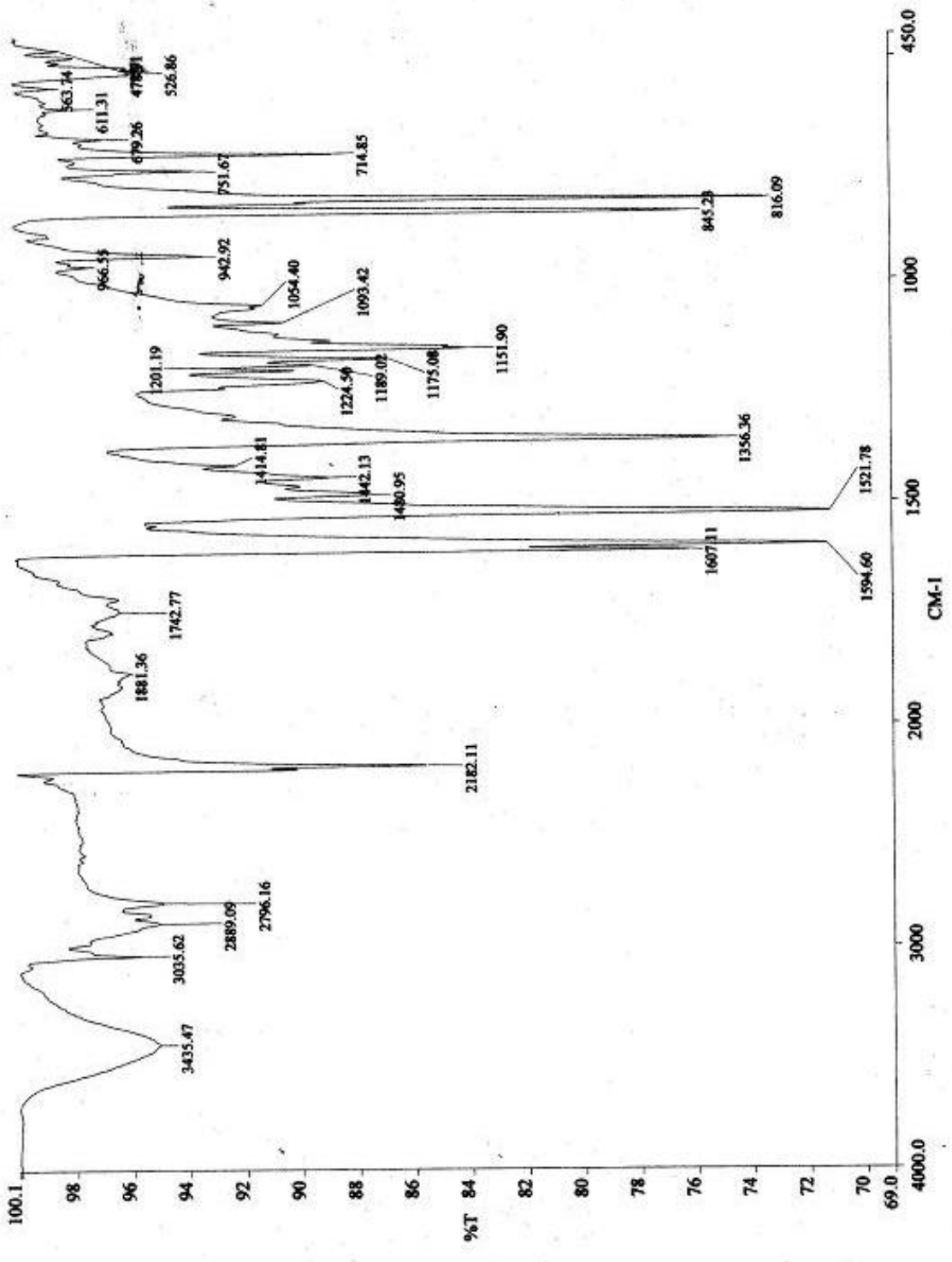
3. High Resolution Mass Spectrum of DMAPEPy

Calculated = 346.12, Obtained = 346.17

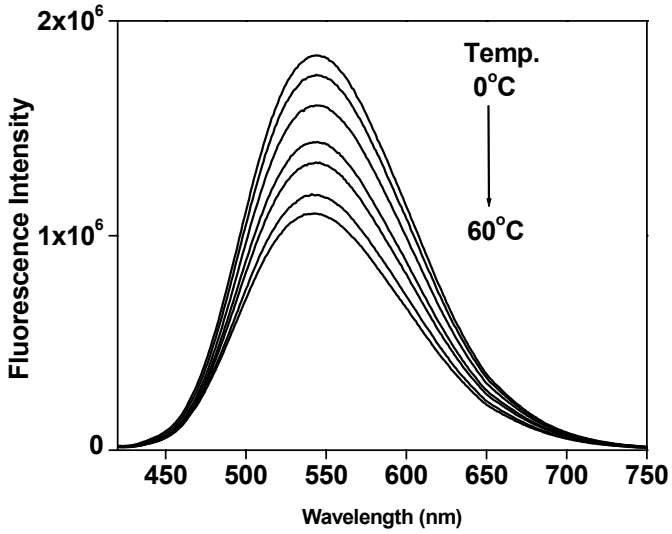


4. FTIR Spectrum of DMAPEPy (KBr pellet)

2182 cm^{-1} (C ≡ C)

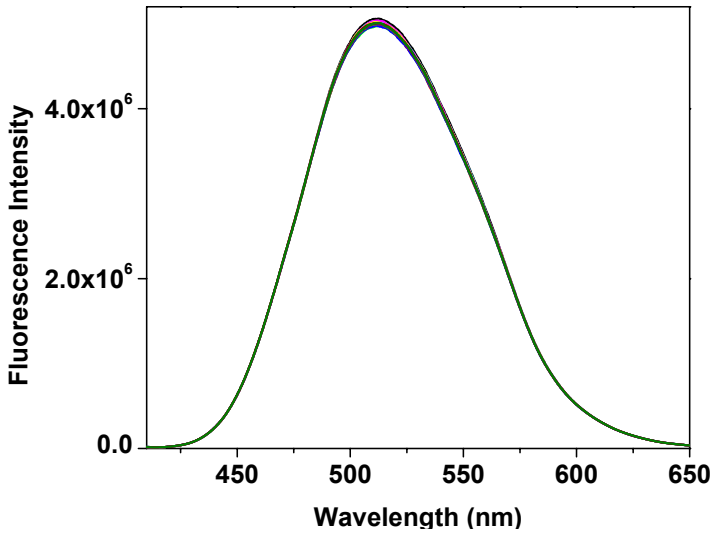


5. Effect of Temperature on the Emission Spectrum of DMAPEPy in Ethylene Glycol



Emission Spectra of DMAPEPy in ethylene glycol as a function of temperature.
(λ_{ex} = 400 nm, λ_{em} = 547 nm)

6. Experiment Showing Photostability of DMAPEPy



Emission spectra of DMAPEPy in ethanol as a function of time under continuous illumination at λ_{ex} = 400 nm for 1 hour. Excitation slit = 10 nm, Emission slit = 2 nm.

7. Dependence of k_f on Solvent Polarity

The solvent dependence of radiative decay rate constant for molecules showing intermolecular or intramolecular charge transfer can be explained by a three state model as suggested by Verhoeven and co-workers[1,2]. According to this model the radiative rate constant is given as

$$\frac{k_f}{n^3 \cdot \nu} = 3.1 \cdot 10^{-7} \cdot \left\{ \left(V \cdot \Delta\mu\right)^2 + 2 \cdot V \cdot V^* \cdot \left[\Delta\mu \cdot \mu^* \cdot \cos(\alpha)\right] \cdot \nu / (\Delta E_1 - \nu) + \left(V^* \cdot \mu^*\right)^2 \cdot \nu^2 / (\Delta E_1 - \nu)^2 \right\}$$

where, n = refractive index of the solvent

$\Delta\mu$ = change in the dipole moment (in Debye) accompanying charge transfer

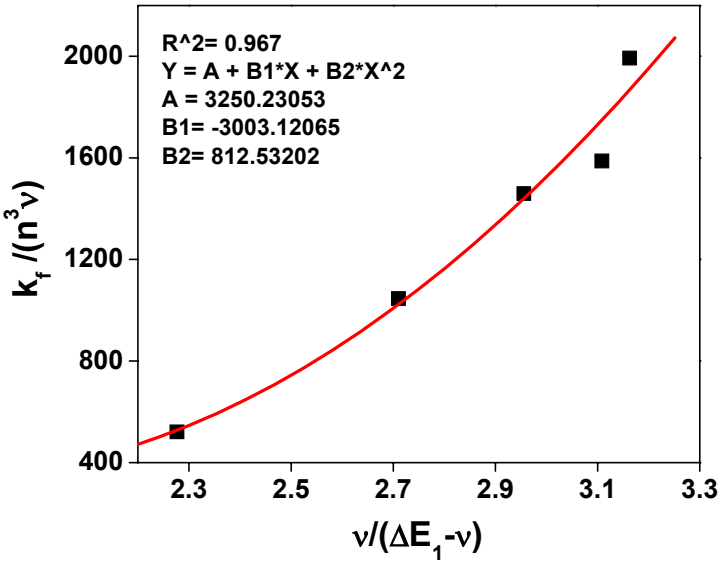
μ^* = transition dipole moment of the unperturbed local DA $\rightarrow$ (DA)* transition

α = angle between μ^* and $\Delta\mu$

ΔE_1= energy gap between the (DA)* and DA states

ν = mean energy of CT fluorescence (in cm^{-1})

The above equation suggests a parabolic dependence of $k_f / (n^3.\nu)$ on $\nu / (\Delta E_1 - \nu)$. In case of DMAPEPy the plot of $k_f/(n^3.\nu)$ versus $\nu/(\Delta E_1 - \nu)$ fits well into a second order polynomial equation when the data for dioxane and benzene are not included in the fit.



Second order polynomial fit for the $k_f /(n^3.\nu)$ versus $\nu/(\Delta E_1 - \nu)$ plot for DMAPEPy in various solvents. The absorption maximum of DMAPEPy in n-hexane was chosen as ΔE_1.

1. M. Bixon, J. Jortner and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1994, 116, 7349-7355.
2. J. W. Verhoeven, T. Scherer, B. wegewijs, R. M. Hermant, J. Jortner, M. Bixon, S. Depaemelaere and F. C. De Schryver, *Recl. Trav. Chim. Pays-Bas*, 1995, 114, 443-448.