

# Cavity size effect on ICT-dual emission of *p*-(*N,N*-dimethylamino)-2-styrylquinoline: complexation with cyclodextrin derivatives

Subramanian Annalakshmi · Kasi Pitchumani

Received: 15 May 2006 / Accepted: 20 October 2006 / Published online: 16 February 2007  
© Springer Science+Business Media B.V. 2007

**Abstract** The effect of cyclodextrin inclusion complex formation on the intramolecular charge transfer (ICT) of the included 4-*N,N*-dimethylamino-2-styrylquinoline (2-StQ-NMe<sub>2</sub>) has been studied in detail. 2-StQ-NMe<sub>2</sub> in presence of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and HP- $\alpha$ - and HP- $\beta$ -CDs predominantly exhibits ICT fluorescence predominantly than the emission from locally excited state, whereas in presence of HP- $\gamma$ -CD the later is observed. In presence of  $\alpha$ -CD, 2:1 complexation of the 2-StQ-NMe<sub>2</sub> is observed in addition to 1:1 complexation. The observed results are explained by the CD cavity size and an active role for the secondary hydroxyl groups present in the wider rim of the CD cavity and also which finds support from absorption, emission, lifetime and molecular modeling studies.

**Keywords** ICT-dual emission · *p*-(*N,N*-Dimethylamino)-2-styrylquinoline · Cyclodextrin derivatives · Hydrogen bonding · Molecular modelling studies

## Introduction

Cyclodextrins (CDs) are water-soluble cyclic oligosaccharides, which has truncated cone-shaped structure [1]. Cyclodextrins are interesting microvessels capable

of embedding appropriately sized fluorophores and thus providing restriction in space [2–4] and a reduced polarity in the near vicinity of the chromophore. Upon inclusion it brings the modification like, fluorescence enhancement [5], quantum yield [6], room temperature phosphorescence [7], energy transfer [8], excimer and exciplex [9, 10] emission and selective protection [5, 11] etc.

The excited state intramolecular charge transfer (ICT) of various organic molecules containing separate electron donor and electron acceptor moieties has been an attractive topic of long term investigations as a possible mechanism for a number of important photochemical and photobiological processes [12]. The dual fluorescence of dimethylamino substituted compound, such as benzonitrile [13], benzanilide [14], and benzimidazole [15] are well studied in presence of CDs.

A series of donor–acceptor stilbenoid compounds are prepared using *N,N*-dimethylamino group as donor and pyridine, quinoline, thiophene are used as acceptor and its photophysical behavior are studied in detail [16]. The photophysical and photochemical properties of some aza-analogues of 1,4-distyrylbenzene, bearing nitrogen heteroatom in the side arene rings, have been investigated [17]. Recently, it has been reported that photoisomerization and photohydration of 3-hydroxystyrylnaphthalenes, the absorbance and emission spectra for 4′substituted-2-styrylquinoline, styrylnaphthalene and neutral and protonated form of *p*-*N,N*-dimethylamino-2-styrylquinoline were studied in various solvents [18–21]. Previous reports on the photophysical modification of NMe<sub>2</sub> substituted compounds in presence of cyclodextrin and the interesting of ICT properties of styrylquinolines have prompted a

**Electronic supplementary material** The online version of this article (doi: 10.1007/s10847-006-9225-8) contains supplementary material, which is available to authorized users.

S. Annalakshmi · K. Pitchumani (✉)  
School of Chemistry, Madurai Kamaraj University, Madurai  
625 021, India  
e-mail: pit12399@yahoo.com

study of fluorescence properties of neutral and protonated form of *p*-(*N,N*-dimethylamino)2-styrylquinoline (2-StQ-NMe<sub>2</sub>) in presence of various CD ( $\alpha$ -,  $\beta$ -,  $\gamma$ -, HP- $\alpha$ -, HP- $\beta$ -, HP- $\gamma$ -, DM- $\beta$ -CD).

## Experimental

Cyclodextrins  $\alpha$ - and  $\gamma$ -CDs (American Maize Products, Indiana),  $\beta$ -CD (Aldrich), HP- $\alpha$ - and HP- $\gamma$ -CDs (DS 4, Nihon Shokuhin Kako Co., Ltd., Japan), HP- $\beta$ -CD (DS 4, randomly hydroxypropylated at primary and secondary hydroxyl groups, Cerestar, USA), DM- $\beta$ -CD (DS 1.8, non-crystallizable, randomly methylated :  $X_2$  – 63.6%,  $X_3$  – 39.6%,  $X_6$  – 64.1% Wacker-Chemie, Germany. 4-*N,N*-dimethylamino-2-styrylquinoline was synthesized according to the procedure given in the literature. Details of experimental procedure [22–24] are given in supplementary information).

## Results and discussion

Absorbance spectral studies of unprotonated and protonated form of 2-StQ-NMe<sub>2</sub> with and without CDs

The absorption and emission maxima for the unprotonated and protonated form of 2-StQ-NMe<sub>2</sub> in presence and absence of cyclodextrins are given in Table 1. In isotropic solvents, 2-StQ-NMe<sub>2</sub> shows two absorption bands in its neutral form at 384 (LW, ICT) and 340 (SW, LE) nms and these two bands are sensitive to the polarity of the medium. The ratio of this band (ICT/

LE) varies when the polarity of the solvents varied (Table 1).

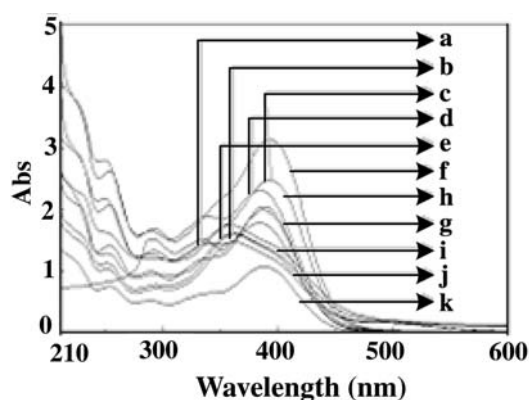
Figure 1 shows the absorption spectrum of 2-StQ-NMe<sub>2</sub> in various solvents and in presence of CDs. In polar solvents the shift in ICT band to longer wavelength may be due to the stabilization by hydrogen bonding of the quinoline nitrogen with polar solvents. By analogy with 3-styrylquinoline [21] it is also likely that 2-styrylquinoline may have presence of two conformational isomers (twisting of the phenyl group with respect to the 2-quinoline moiety) (Scheme 1).

When the neutral molecule is included into the CD cavity, a pronounced change in the absorption spectrum is noticed. UV absorption spectra of 2-StQ-NMe<sub>2</sub> in presence of various CDs are given in Fig. 1, which shows that in presence of  $\alpha$ -,  $\beta$ -, HP- $\beta$ - and DM- $\beta$ -CDs, magnitude of the absorption is higher at 340 nm band (LE band) than the ICT band, whereas the ICT band is more intense in presence of  $\gamma$ - and HP- $\alpha$ , and - $\gamma$ -CDs. In presence of all the CDs, there is a small red shift (about 2–10 nm) in both the LE and ICT band. The increase in intensity of ICT absorption is attributed to stabilization of this state by hydrogen bonding with CD hydroxyl groups. In a control experiment with permethylated- $\beta$ -CD, ICT/LE ratio is 0.699 and this also provides strong support to stabilization of ICT state by hydrogen bonding with CD-hydroxyl groups.

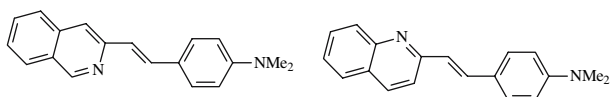
Upon protonation of 2-StQ-NMe<sub>2</sub>, the absorption maxima for ICT at 398 nm undergoes a large red shift to 506 nm and on the other hand, LE band undergoes a small blue shift to 315 nm (Fig. 2). Large shift is attributed to the quinoline nitrogen atom is protonated than the *N,N*-dimethylaniline site. When the quinoline

**Table 1** Absorbance and emission wavelengths (nm) of unprotonated and protonated forms of 2-StQ-NMe<sub>2</sub> in presence of isotropic solvent and in presence of cyclodextrins

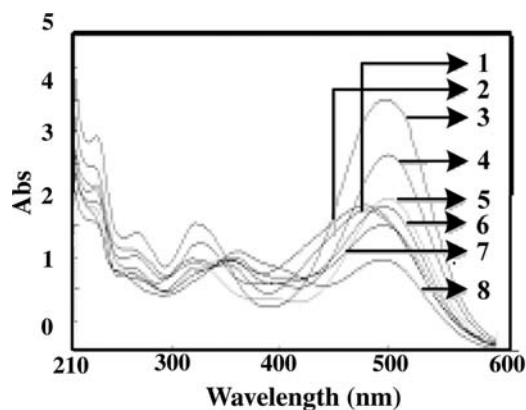
Medium	Wavelength (nm)										
	Unprotonated						Protonated				
	$\lambda_{\text{abs}}$			$\lambda_{\text{emi}}$			$\lambda_{\text{abs}}$			$\lambda_{\text{emi}}$	
	LW	SW	LW/SW	LW	SW	LW/SW	L	W	SW	LW/SW	LW (alone)
ACN	384	340	1.32	578	528	0.84	508	310	–	–	630
MeOH	394	345	2.50	584	532	0.48	506	315	–	–	631
Toluene	388	334	1.78	–	480	–	–	–	–	–	–
ACN/Water	386	332	1.15	588	538	–	–	316	–	–	–
$\alpha$ -CD	398	360	0.82	594	538	1.41	504	312	1.84	–	632
$\beta$ -CD	398	362	0.85	587	538	1.09	500	312	1.78	–	634
$\gamma$ -CD	398	364	1.76	584	530	4.56	496	312	1.86	–	635
HP- $\alpha$ -CD	394	362	1.22	602	536	1.67	501	312	–	–	630
HP- $\beta$ -CD	386	360	0.82	590	544	1.17	–	–	1.05	–	–
HP- $\gamma$ -CD	390	300	1.45	596	538	0.72	500	356	–	–	–
DM- $\beta$ -CD	384	362	0.77	578	528	1.18	–	–	–	–	–



**Fig. 1** Absorption spectra of 2-StQ-NMe<sub>2</sub> (unprotonated form) in presence of (a) DM- $\beta$ -, (b)  $\beta$ -, (c) HP- $\alpha$ - CDs (d) Methanol, (e) HP- $\beta$ -, (f)  $\gamma$ -CDs (g) 5% ACN-95% water, (h) Toluene (i) HP- $\gamma$ -CD (j)  $\alpha$ -CD and (k) ACN, [sub] =  $7.5 \times 10^{-4}$  M, [CD] =  $1.5 \times 10^{-4}$  M



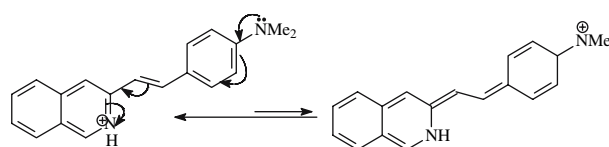
**Scheme 1** Two different conformational isomers of 2-StQ-NMe<sub>2</sub>



**Fig. 2** Absorption spectra of protonated form of 2-StQ-NMe<sub>2</sub> in presence of (1)  $\alpha$ -CD, (2) ACN, (3) ACN/Water, (4)  $\beta$ -CD, (5)  $\gamma$ -CD, (6) HP- $\gamma$ -CD and in (7) Methanol

is protonated, the electron pulling ability will be stronger and will show a larger red-shift in the charge transfer (CT) absorption (398–506) is observed. The blue shift of LE band upon protonation arises due to the delocalization as given below (Scheme 2).

The protonated form of 2-StQ-NMe<sub>2</sub>, in presence of the CDs shows no difference in the absorption maximum of both ICT as well as LE bands, but the magnitude of absorption increases, when the CD concentration is increased (Fig. 2).



**Scheme 2** Protonated and unprotonated form of 2-StQ-NMe<sub>2</sub>

Emission data for unprotonated and protonated forms of 2-StQ-NMe<sub>2</sub> with and without CDs

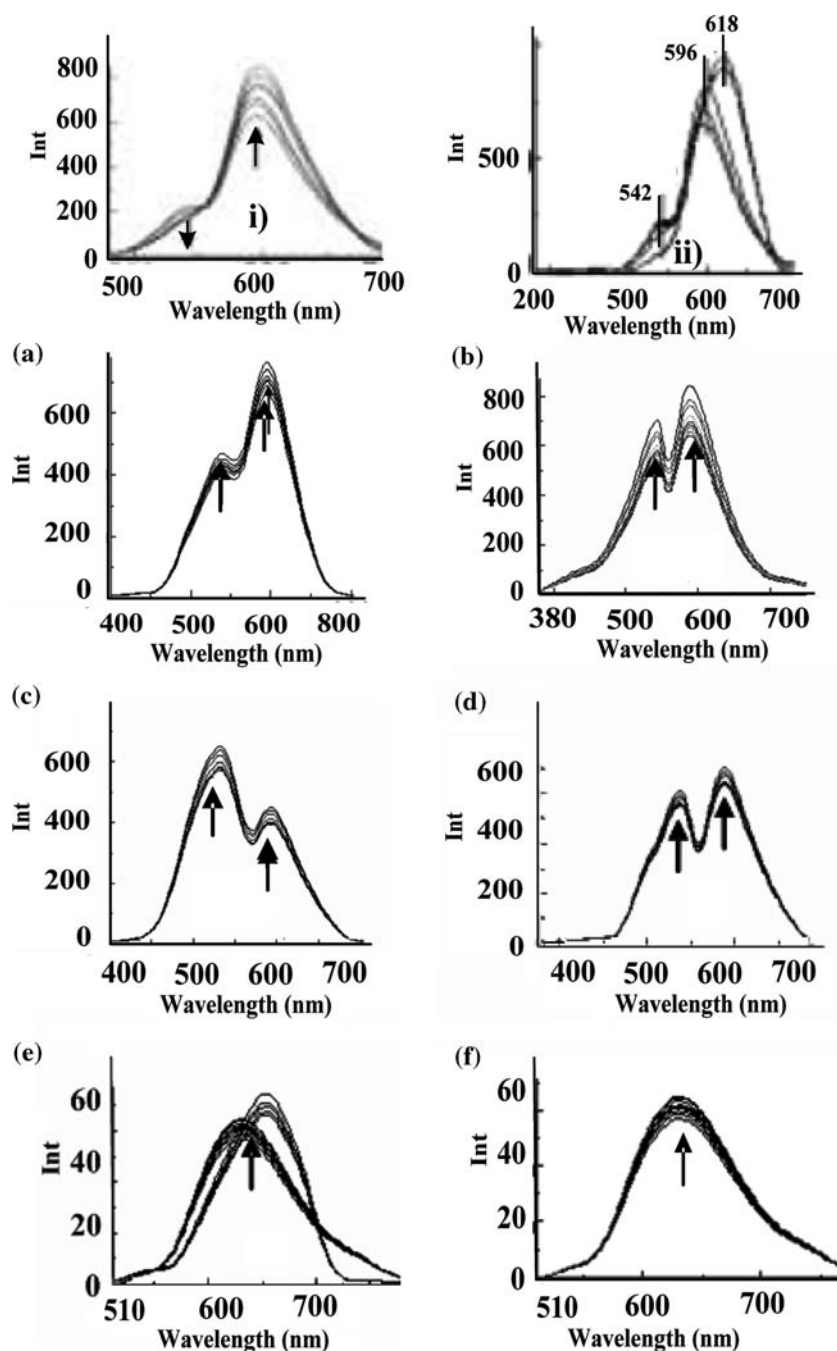
Emission spectra of neutral and protonated forms of 2-StQ-NMe<sub>2</sub> in presence of various solvents are studied. Dual fluorescence is observed in moderately polar solvents, whereas only emission from the LE state is observed in nonpolar solvents. The LE band obtained in nonpolar (toluene) medium gets red shifted from 480 nm to 532 nm in presence of methanol. This may be presumably due to increased hydrogen bonding interactions of polar solvents with quinoline nitrogen atom. When the 2-StQ-NMe<sub>2</sub> is protonated with a small excess of acid concentration, it leads to the formation of quinoline-ring protonated species and the emission spectra (given in Fig. 3, 4, supplementary information) show only a broad band structures at 630 nm, indicating clearly that only ICT state and its emission is much more significant and LE band is totally suppressed. It is relevant to recall that it undergoes large shift in absorption also (384–508) as well as in emission spectra (608–630 nm). Emission spectra of neutral and protonated form of 2-StQ-NMe<sub>2</sub> in aqueous solution containing varying concentrations of  $\alpha$ -CD are shown in Figs. 3a–f. Addition of  $\alpha$ -CD causes an enhancement in the emission wavelength to 594 nm for the ICT band. The LE emission at 538 nm decreases as the CD concentration increases. Further increase in the  $\alpha$ -CD concentration above  $\sim 7.5 \times 10^{-3}$  M, the  $\lambda_{\text{emi}}$  is shifted from the 596 nm to 618 nm indicating the formation of higher order complexes, which is also confirmed from the Jobs plot (Fig. 5, supplementary information)

From the dependence of the ICT emission intensity with  $\alpha$ -CD concentration equilibrium constants are calculated using Eq. 1.

$$\frac{F}{F_0} = \frac{1 + F_1/F_0 K_1 [CD]_0 + F_2/F_0 K_1 K_2 [CD]_0^2}{(1 + K_1 [CD]_0 + K_1 K_2 [CD]_0^2)} \quad (1)$$

The fluorescence ( $F/F_0$  versus CD) intensities are plotted and fitted into Eq. 1 and this gives formation constant values ( $K_1$  and  $K_2$ ) (Table 3, supplementary

**Fig. 3** Emission spectra of neutral form of 2-StQ-NMe<sub>2</sub> in presence of (i) and (ii) in presence of  $\alpha$ -CD, (a) HP- $\alpha$ -CD, (b) HP- $\beta$ -CD, (c) Hp- $\gamma$ -CD), (d) DM- $\beta$ -CD, (e) Protonated form of 2-StQ-NMe<sub>2</sub> in presence of  $\alpha$ -CD (f)  $\beta$ -CD



information). As the double reciprocal plot of  $1/(F/F_0-1)$  vs.  $1/[\alpha\text{-CD}]$  is not linear the formation of 2:1 complexes are inferred.

Lifetime and binding constants values for 2-StQ-NMe<sub>2</sub> with and without CDs

The lifetime analysis also indicates that the presence of two different species in various solvents (Table 2) Lifetime studies for this substrate in different solvent

indicates that two different conformers are present during shorter wavelength of excitation. This may be due to the existence of two different species arising from hindered twisting of the quasi single bond. The different species may also arise from the different conformational isomer (discussed earlier).

Lifetime analysis from the Time correlated single photon counting (TCSPC) technique shows that in presence of  $\alpha$ -CD, three different components (triexponential decay curve), with the lifetime values ( $\tau$ , ns)

**Table 2** Lifetime data for 2-StQ-Nme2 in presence of various media

Lifetime data for the unprotonated form of 2-StQ-NMe <sub>2</sub> in presence of solvent and CDs								
Medium	$\lambda_{\text{exe}}$	Life time (ns)			Relative Amplitude			$\chi^2$
		I	II	III	I	II	III	
ACN	528	0.686	0.186	–	64.2	35.8		1.174
CH <sub>2</sub> Cl <sub>2</sub>	506	0.392	0.12	–	57.7	48.3		1.298
MeOH	532	0.106	0.459	–	82.8	17.2		1.333
Toluene	480	0.749	0.228	–	67.3	32.7		1.847
ACN/H <sub>2</sub> O	540	0.221	0.956	–	69.1	30.9		1.468
$\alpha$ -CD	587	0.242	0.69	1.89	42.1	19.8	38.1	
$\beta$ -CD	587	0.251	1.58		39.3	60.6		1.159
$\gamma$ -CD	587	0.245	8.31		29.1	70.9		1.41
$\alpha$ -CD	543	0.23	0.71		37.3	62.7		1.112
$\beta$ -CD	543	0.599	1.62		49.9	50.1		1.35
$\gamma$ -CD	543	0.245	2.92		43	57		1.159
Lifetime data for the protonated form of 2-StQ-NMe <sub>2</sub> in presence of solvent and CDs								
ACN	630	0.029	1.19	–	22.8	72.2	–	1.13
MeOH	632	0.035	0.546		12.5	87.5	–	1.29
ACN /H <sub>2</sub> O	631	0.029	1.08		10.4	89.6	–	1.49
$\alpha$ -CD	634,652	0.966	0.34	6.65	8.4	28.8	62.2	1.11
$\beta$ -CD	635	0.116	0.35	6.59	10.7	17.5	72	1.19
$\gamma$ -CD	630	0.104	0.33	8.12	20.2	9.33	69.9	1.3

$\tau_1 = 0.242$ ,  $\tau_2 = 0.690$  and  $\tau_3 = 1.89$  respectively are obtained for 587 nm emission (Table 2), which is indicative of the presence of three different species in presence of  $\alpha$ -CD.  $\tau_1$  and  $\tau_2$  may be due to the two different conformers discussed earlier. A longer lived component is also present in  $\alpha$ -CD, which is attributed to the presence of CD-complexed 2-StQ-NMe<sub>2</sub>. Comparison of lifetimes in solution and in presence of CDs shows that excitation of band ( $\lambda_{\text{exi}} = 384$  nm,  $\lambda_{\text{emi}} = 543$  nm) shows two lifetime components, similar to that observed in solution. In all other CDs, a component with much longer lifetime is noticed which is attributed to that of CD-complexed 4-*N,N*-dimethyl-2-styrylquinoline. The lifetime value of the 2-StQ-NMe<sub>2</sub> is higher with  $\gamma$ -CD (in accordance with binding constants also) indicating that the complex stability is more in presence of  $\gamma$ -CD.

## Conclusion

Absorption and emission studies of 4-*N,N*-dimethylamino-2-styrylquinoline (2-StQ-NMe<sub>2</sub>) in both unprotonated and protonated forms in presence of various CDs namely,  $\alpha$ -,  $\beta$ -,  $\gamma$ -, HP- $\alpha$ -, HP- $\beta$ -, HP- $\gamma$ -CDs and DM- $\beta$ -CD are recorded in aqueous solution. Dual fluorescence is observed in most cases. Fluorescence lifetime is measured for the formation of inclusion complexes between 2-StQ-NMe<sub>2</sub> and CD. Equilibrium constants are calculated for the ground as well as in the

excited states. Based on the experimental observations (fluorescence, lifetime analysis and molecular modeling- Fig. 4 in supplementary information), it is concluded that the more polar ICT emission is favored in presence of CDs as it is stabilized by the secondary hydroxyl groups present in the CD cavity.

**Acknowledgements** Financial assistance from Council of Scientific and Industrial Research (CSIR), New Delhi is gratefully acknowledged.

## References

- (a) Bender, M.L., Komiyama, M.: Cyclodextrin Chemistry. Springer-Verlag, Berlin, New York (1978); (b) Szejtli, J.: Cyclodextrins and Their Inclusion Complexes. Akademiai Kiado, Budapest (1982)
- Szejtli, J.: Utilization of cyclodextrins in industrial products and processes. *J. Mater. Chem.* **7**, 575–587 (1997)
- Takahashi, K.: Organic reactions mediated by cyclodextrins. *Chem. Rev.* **98**, 2013–2034 (1998)
- Baglolle, K.N., Boland, P.G., Wagner, B.D.: Fluorescence enhancement of curcumin upon inclusion into parent and modified cyclodextrins. *J. Photochem. Photobiol. A: Chem.* **173**, 230–237 (2005)
- Postor, I., Marino, A.D., Mendicuti, F.: Complexes of dihexyl 2,6-naphthalenedicarboxylate with  $\alpha$ - and  $\beta$ -cyclodextrins: Fluorescence and molecular modeling. *J. Photochem. Photobiol. A: Chem.* **173**, 238–247 (2005)
- Dewi, Y., Tomoko, S., Keita, H., Hisakazu, M., Ueno, A.: Double naphthalene-tagged cyclodextrin-peptide capable of exhibiting guest-induced naphthalene excimer fluorescence. *Macromol. Rapid Commun.* **23**, 11–15 (2002)

7. Kuijt, J., Ariese, F., Brinkman, U.A.Th., Gooijer, C.: Room temperature phosphorescence in the liquid state as a tool in analytical chemistry. *Anal. Chim. Acta.* **488**, 135–137 (2003)
8. Panja, S., Chakravorti, S.: Photophysics of 4-(*N,N*-dimethylamino)cinnamaldehyde/ $\alpha$ -cyclodextrin inclusion complex. *Spectroc. Acta Part A* **58**, 113–122 (2002)
9. Tormo, L., Douhal, A.: Caging anionic structure of a proton transfer dye in a hydrophobic nanocavity with a cooperative H-bonding. *J. Photochem. Photobiol. A: Chem.* **173**, 358–364 (2005)
10. Pitchumani, K., Vellayappan, M.: Complex formation of nitrobenzoic acids and some naphthalene derivatives with  $\beta$ -cyclodextrin. *J. Incl. Phenom. Mol. Recogn. Chem.* **14**, 157–162 (1992)
11. Cox, G.S., Turro, N.J.: Methyl salicylate fluorescence as a probe of the geometry of complexation to cyclodextrins. *Photochem. Photobiol.*, **40**, 185–188 (1984)
12. Saigusa, H., Iwase, E., Nishimura, M.: Intramolecular charge-transfer dynamics in *p*-dimethylaminobenzonitrile: acetonitrile clusters. *J. Phys. Chem. A.* **107**, 3759–3763 (2003)
13. Yoshizawa, T., Iwaki, Y., Osaka, N., Nakabayashi, T., Zachariasse, K.A., Ohta, N.: External electric field effects on absorption, fluorescence and phosphorescence spectra of 4-(dimethylamino)benzonitrile in a polymer. *J. Phys. Chem. B.* **108**, 19132–19139 (2004)
14. Zhang, X., Wang, C.J., Liu, L.H., Jiang, Y.B.: Reversal of the intramolecular charge transfer in *p*-dimethylaminobenzanilides by amido anilino substitution. *J. Phys. Chem. B.* **106**, 12432–12440 (2002)
15. (a) Krishnamoorthy, G., Dogra, S.K.: Dual fluorescence of 2-(4'-*N,N*-dimethylaminophenyl)benzimidazole: effect of  $\beta$ -cyclodextrin and pH. *J. Photochem. Photobiol. A: Chem.* **123**, 109–119 (1999); (b) Das, S.K.: Inclusion complexation of 2-(4'-*N,N*-dimethylaminophenyl)-1*H*-naphth[2,3-*d*]imidazole by  $\beta$ -cyclodextrin: effect on the twisted intramolecular charge transfer emission. *Chem. Phys. Lett.* **361**, 21–28 (2002)
16. Chen, C.Y., Ho, J.H., Wang, S.L., Ho, T.I.: Excimer and intramolecular charge transfer chemiluminescence from electrogenerated ion radicals of donor–acceptor stilbenoids. *Photochem. Photobiol. Sci.* **2**, 1232–1236 (2003)
17. Spalletti, A.: Photochem. Conformer-specific and two-fold adiabatic photoisomerization of *ZZ*-1,4-di-(2-quinolylolethyl)benzene. *Photobiol. Sci.* **3**, 695–699 (2004)
18. Bandini, E., Bortolus, P., Manet, I., Monti, S., Galiazz, G., Gennari, G.: Photoisomerization and photohydration of 3-hydroxystyrylnaphthalenes. *Photochem. Photobiol. Sci.* **4**, 862–868 (2005)
19. Wang, S.L., Ho, T.I.: Emission spectra studies on the hydrogen-bonding complexes between *p*-methoxy-2-styrylquinoline and acids. *Spectroc Acta Part A* **57**, 361–366 (2001)
20. Wang, S.L., Lee, T.C., Ho, T.I.: Excited state proton transfer and steric effect on the hydrogen bonding interaction of the styrylquinoline system. *J. Photochem. Photobiol. A: Chem.* **151**, 21–26 (2002)
21. Gennari, G., Galiazzo, G., Bortolus, P.: Solvent effects on the emissive properties of *trans*-3-styrylquinoline in neutral and acidic solutions. *J. Photochem.* **35**, 177–188 (1986)
22. Tahara, R., Morozuni, T., Nakamura, T.: Photoisomerization of azobenzocrown ethers. Effect of complexation of alkaline earth metal ions. *J. Phys. Chem.* **101**, 7736–7743 (1997)
23. Discover Users Guide, Accelrys Inc. (2001)
24. Kaslow, C.E., Stayner, R.D.: The preparation and properties of inorganic coordination compounds. I. The action of some organic amines upon dichloro-diethylenediamine cobaltic chloride. *J. Am. Chem. Soc.* **67**, 171–175 (1945)