Supplementary Material (ESI) for Photochemical & Photobiological Sciences
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Excited State Intramolecular Proton Transfer (ESIPT) from Phenol to Nitrogen and Carbon in (2-Hydroxyphenyl)pyridines

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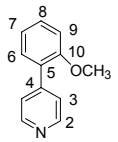
Preparation of 4-(2-methoxyphenyl)pyridine

To a solution of 500 mg 4-bromopyridine hydrochloride (2.57 mmol) in 10 mL of H_2O, a solution of Na_2CO_3 was added (0.5 g / 40 mL H_2O). The mixture was extracted with CH_2Cl_2 and the extracts were dried over anhydrous $MgSO_4$. To the extracts, 10mL of DME was added and solvent was almost completely removed. To the residue 10 mL of DME was added and solvent was again almost completely removed. The residue was transferred to a two-neck flask (connected to a reflux condenser and nitrogen inlet) and diluted by 30 mL of DME. The apparatus was purged by N_2 and 35 mg of $Pd(PPh_3)_4$ was added. A solution of 600 mg of potassium *tert*-butoxyde (5.20 mmol) in 5 mL of *tert*-butanol was prepared under N_2. To the solution of base, 390 mg of 2-methoxyphenyl boronic acid (2.57 mmol) was added, followed by 1-2 mL of DME, to completely dissolve the boronic acid. The mixture of boronic acid and base was added by a syringe to the reaction mixture. Reaction was heated at the temperature of reflux under N_2 for 12 hours. To the cooled mixture, 30 mL of water was added and extractions with CH_2Cl_2 were carried out. Collected extracts were dried over anhydrous $MgSO_4$. Solvent was evaporated and the residue chromatographed on a column with silica gel using hexane / EtOAc (7:3) as eluent. The product was isolated (370 mg, 77 %) in form of colorless crystals.



^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.60 (broad d, 2H, *J* = 3.8 Hz, H-2), 7.45 (d, 2H, *J* = 5.9 Hz, H-3), 7.37 (ddd, 1H, *J* = 2.0 Hz, *J* = 7.0 Hz, *J* = 8.0 Hz, H-8), 7.32 (dd, 1H, *J* = 1.5 Hz, *J* = 7.5 Hz, H-6), 7.04 (dd, 1H, *J* = 7.5 Hz, *J* = 7.0 Hz, H-7), 6.99 (d, 1H, *J* = 8.0 Hz, H-9), 3.82 (s, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 156.71 (s, C-10), 149.61 (d, C-2), 146.55 (s, C-4), 130.65 (d, C-8), 130.32 (d, C-6), 127.82 (s, C-5), 124.51 (d, C-7), 121.24 (d, C-3), 111.58 (d, C-9), 55.72 (q, CH3);

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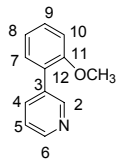
Preparation of 3-(2-methoxyphenyl)pyridine

In a two-neck flask equipped with condenser and N_2 inlet, 200 mg of pyridine-3-boronic acid (1.63 mmol) was mixed with 300 mg (210 μL; 1.63 mmol) of 2-bromoanisole. To the mixture, 20 mL dioxane and 20 mL of 2M aqueous solution of K_2CO_3, was added. The apparatus was purged with N_2, 32 mg of $Pd(PPh_3)_4$ was added, and apparatus was again purged with N_2. Reaction mixture was heated at the temperature of reflux under N_2 for 24 hours. To the cooled mixture, 30 mL of water was added and extractions with CH_2Cl_2 were carried out. Collected extracts were dried over anhydrous $MgSO_4$. Solvent was evaporated and the residue chromatographed on a column with silica gel using CH_2Cl_2 / EtOAc (1:1) as eluent. The product was isolated (150 mg, 49 %) in form of colorless crystals.



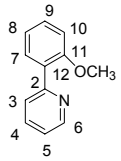
^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.75 (broad s, 1H, H-2), 8.53 (broad s, 1H, H-6), 7.85 (dd, J = 1.8 Hz, J = 6.1 Hz, H-4), 7.26-7.40 (m, 3H, H-5, H-7 and H-9), 7.04 (dd, 1H, J = 7.1 Hz, J = 7.3 Hz, H-8), 7.00 (d, 1H, J = 8.1 Hz, H-10), 3.81 (s, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.21 (d), 147.89 (d), 137.23 (d), 130.88 (d), 129.85 (d), 121.29 (d), 111.52 (d), 55.76 (q), all the signals were not seen due to the small quantity of the sample;

Preparation of 2-(2-methoxyphenyl)pyridine

In a two-neck flask equipped with condenser and N_2 inlet, 500 mg (3.29 mmol) of 2-methoxyphenyl boronic acid was dissolved in 20 mL of 2M aqueous solution of K_2CO_3. To the solution, 480 mg (3.00 mmol) of 2-bromopyridine in 20 mL of dioxane, was

added. The apparatus was purged with N_2, 70 mg of $Pd(PPh_3)_4$ was added, and apparatus was again purged with N_2. Reaction mixture was heated at the temperature of reflux under N_2 for 18 hours. To the cooled mixture, 30 mL of water was added and extractions with CH_2Cl_2 were carried out. The collected extracts were dried over anhydrous $MgSO_4$. Solvent was evaporated and the residue was chromatographed on a column with silica gel using CH_2Cl_2 / EtOAc (7:3) as eluent. The product was isolated (550 mg, 99 %) in form of yellowish oil.



^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.68 (d, 1H, *J* = 4.8 Hz, H-6), 7.79 (d, 1H, *J* = 8.0 Hz, H-7), 7.73 (dd, 1H, *J* = 1.7 Hz, *J* = 7.7 Hz, H-3), 7.68 (ddd, 1H, *J* = 1.6 Hz, *J* = 7.5 Hz, *J* = 8.2 Hz, H-9), 7.36 (ddd, 1H, *J* = 1.8 Hz, *J* = 7.7 Hz, *J* = 7.7 Hz, H-4), 7.19 (ddd, 1H, *J* = 1.4 Hz, *J* = 4.4 Hz, *J* = 6.1 Hz, H-5), 7.06 (dd, 1H, *J* = 7.5 Hz, *J* = 8.0 Hz, H-8), 6.99 (d, 1H, *J* = 8.2 Hz, H-10), 3.84 (s, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 157.14 (s, C-11), 156.24 (s, C-2), 149.47 (d, C-6), 135.99 (d, C-4), 131.38 (d), 130.22 (d), 125.38 (d), 121.91 (d), 121.27 (d), 111.59 (d, C-10), 55.84 (q), one singlet was not seen;

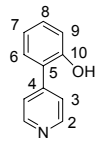
Cleavage of the methyl group by use of BBr_3 – general procedure

The methoxy compound was dissolved in dichloromethane and the solution was cooled to 0 °C by ice- water bath. By use of a syringe a dichloromethane solution (1M) of 5 equivalents of BBr_3 per equivalent of methoxy compound was added dropvise under nitrogen. The ice bath was removed and reaction mixture stirred at rt for additional 2 hours under nitrogen. Reaction was quenched by addition of water and layers were separated. The water layer was washed two more times by use of dichloromethane. The water layer was neutralized to pH 7 by use of sodium bicarbonate and extracted by ethyl

acetate. Collected extracts were dried over anhydrous $MgSO_4$ and solvent was removed. White powder that was obtained was purified further by several recrystalizations using methanol.

4-(2-hydroxyphenyl)pyridine (**1c**)

Starting from 250 mg of 4-(2-methoxyphenyl)pyridine (1.35 mmol) reaction furnished 200 mg (86 %) of the product.



White crystals; ^{1}H NMR (CD_3OD, 300 MHz) δ 8.51 (broad s, 2H, H-2), 7.69 (d, 2H, *J* = 5.0 Hz, H-3), 7.37 (dd, 1H, *J* = 1.5 Hz, *J* = 8.0 Hz, H-6), 7.25 (ddd, 1H, *J* = 1.5 Hz, *J* = 7.5 Hz, *J* = 8.0 Hz, H-8), 6.95 (dd, 1H, *J* = 7.5 Hz, *J* = 8.0 Hz, H-7), 6.93 (d, 1H, *J* = 7.5 Hz, H-9), OH was exchanged by D;

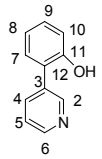
^{13}C NMR (CD_3OD, 75 MHz) *δ* 156.14 (s), 149.52 (d), 131.44 (d), 131.25 (d), 126.11 (s), 125.80 (s), 121.15 (d), 117.27 (d), one doublet was not seen;

^{1}H NMR ($(CD_3)_2CO$, 300 MHz) δ 9.00 (broad s, OH), 8.59 (broad s, 2H, H-2), 7.62 (d, 2H, *J* = 5.9 Hz, H-3), 7.40 (dd, 1H, *J* = 1.5 Hz, *J* = 7.8 Hz, H-6), 7.26 (ddd, 1H, *J* = 1.5 Hz, *J* = 7.5 Hz, *J* = 7.8 Hz, H-8), 7.04 (d, 1H, *J* = 7.5 Hz, H-9), 6.97 (dd, 1H, *J* = 7.2 Hz, *J* = 7.5 Hz, H-7);

^{13}C NMR ($(CD_3)_2CO$, 75 MHz) *δ* 155.55 (s, C-10), 150.23 (d, C-2), 147.25 (s, C-4), 131.12 (d, C-6/8), 130.89 (d, C-6/8), 126.25 (s, C-5), 124.84 (d, C-3), 121.03 (d, C-7), 117.25 (d, C-9);

3-(2-hydroxyphenyl)pyridine (**1b**)

Starting from 150 mg (0.81 mmol) of 3-(2-methoxyphenyl)pyridine reaction furnished 130 mg (93 %) of the product.



^{1}H NMR ($(CD_3)_2CO$, 300 MHz) δ 8.82 (broad s, 1H, H-2), 8.52 (broad s, 1H, H-6), 8.08 (d, 1H, *J* = 7.7 Hz, H-4), 7.41 (dd, 1H, *J* = 5.0 Hz, *J* = 7.7 Hz, H-5), 7.35 (dd, 1H, *J* = 1.0

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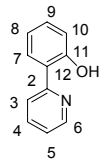
Hz, *J* = 7.7 Hz, H-7), 7.24 (ddd, 1H, *J* = 1.0 Hz, *J* = 7.3 Hz, *J* = 8.0 Hz, H-8), 7.03 (d, 1H, *J* = 8.0 Hz, H-10), 6.92 (dd, 1H, *J* = 7.3 Hz, *J* = 7.7 Hz, H-8), OH was not seen;
^{13}C NMR ($(CD_3)_2CO$,75 MHz) δ 155.36 (s, C-11), 150.74 (d, C-2), 148.42 (d, C-6), 137.28 (d, C-4), 131.36 (d, C-9), 130.27 (d, C-7), 123.93 (s, C-12), 121.11 (d, C-8), 117.06 (d, C-10), all the signals were not seen due to the small quantity of the sample;

2-(2-hydroxyphenyl)pyridine (**1a**)

Starting from 550 mg (2.97 mmol) of 2-(2-methoxyphenyl)pyridine reaction furnished 100 mg (20 %) of the product.



^{1}H NMR ($(CD_3)_2CO$, 300 MHz) δ 14.14 (s, 1H, OH), 8.62 (d, 1H, *J* = 5.0 Hz, H-6), 8.18 (d, 1H, *J* = 8.2 Hz, H-7), 8.02 (ddd, 1H, *J* = 1.4 Hz, *J* = 7.6 Hz, *J* = 8.0 Hz, H-4), 7.97 (dd, 1H, *J* = 1.3 Hz, *J* = 7.6 Hz, H-3), 7.42 (ddd, 1H, *J* = 1.3 Hz, *J* = 5.0 Hz, *J* = 7.6 Hz, H-5), 7.30 (ddd, *J* = 1.4 Hz, *J* = 7.2 Hz, *J* = 8.0 Hz, H-9), 6.92 (d, 1H, *J*= 8.0 Hz, H-10), 6.90 (dd, 1H, *J* = 7.2 Hz, *J* = 8.2 Hz, H-8);
^{13}C NMR ($(CD_3)_2CO$,75 MHz) δ 161.01 (s, C-11), 158.67 (s, C-2), 146.95 (d, C-6), 139.26 (d, C-4), 132.21 (d, C-7), 127.37 (d, C-9), 122.87 (d, C-3), 120.24 (d, C-5), 119.67 (s, C-12), 119.52 (d, C-8) 119.07 (d, C-10);

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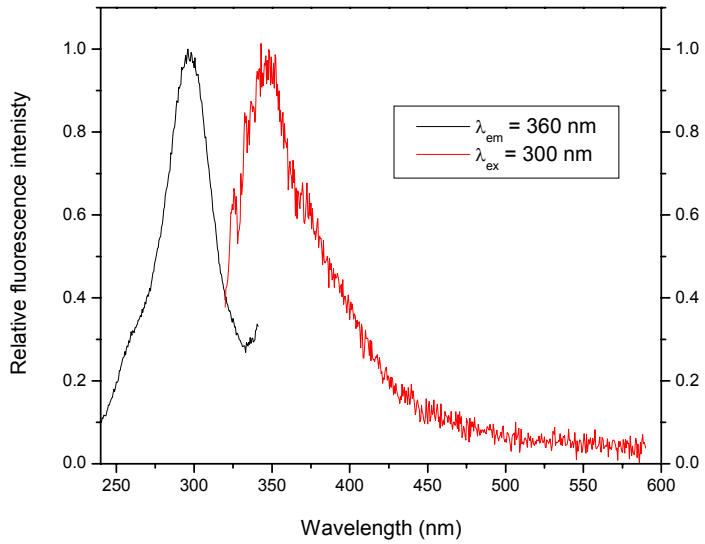
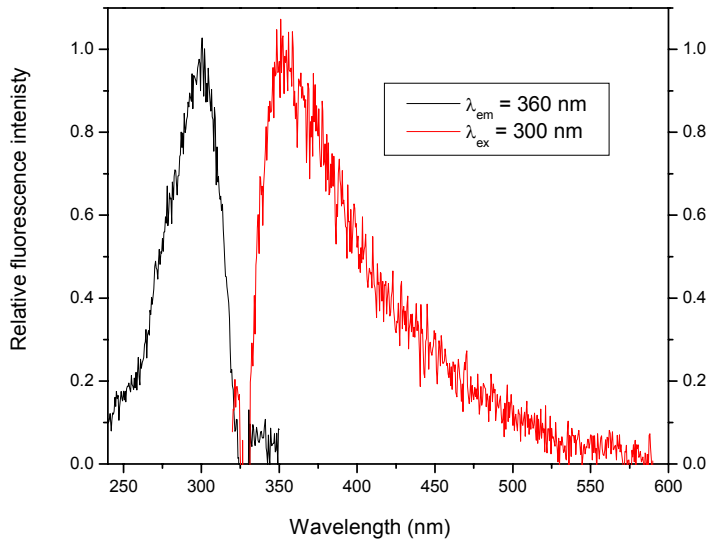
Excitation and emission spectra of 2-(2'-hydroxyphenyl)pyridine (1a) in acetonitrile (above) and methanol (bellow)





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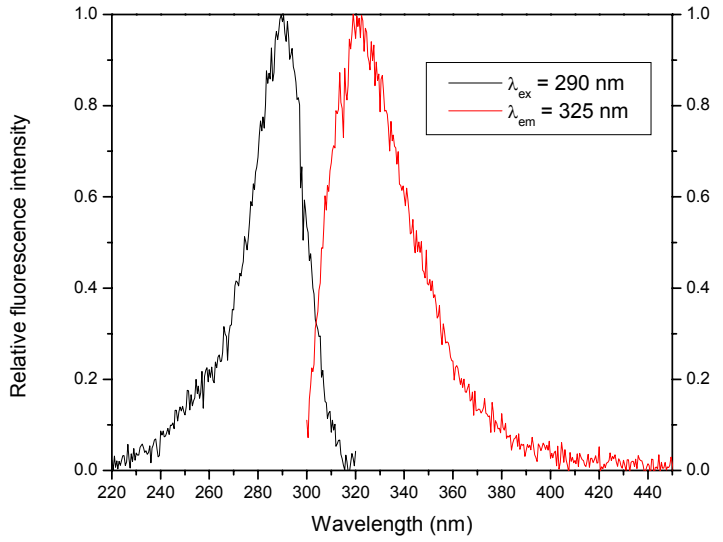
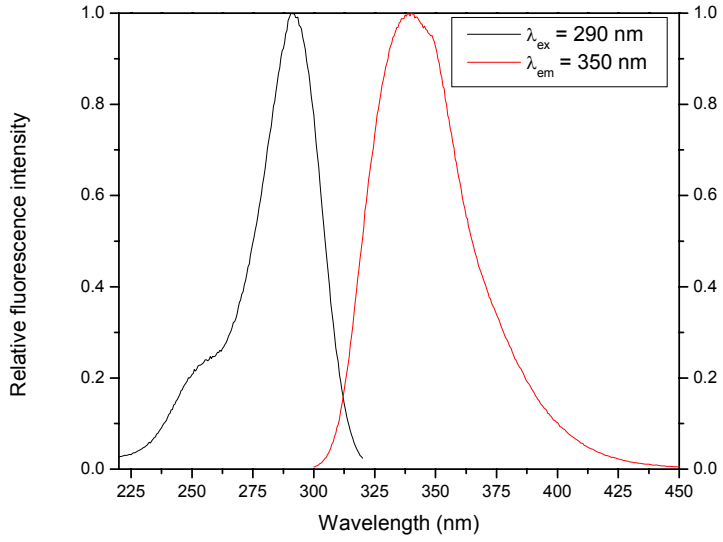
Excitation and emission spectra of 3-(2'-hydroxyphenyl)pyridine (1b) in cyclohexane (above) and acetonitrile (bellow)





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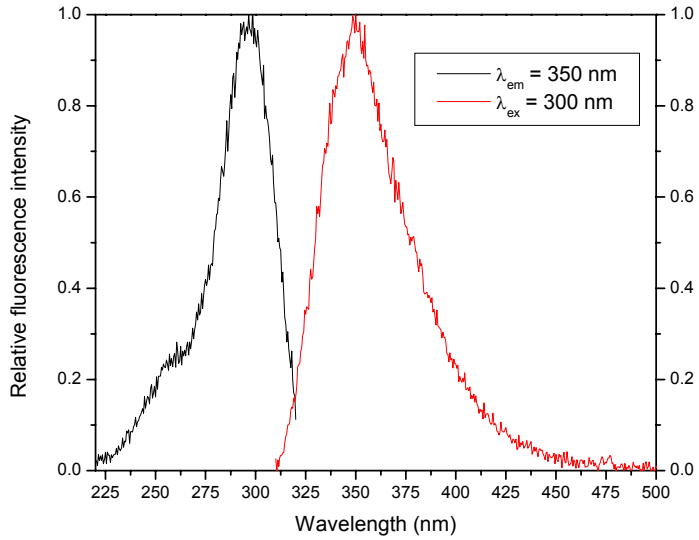
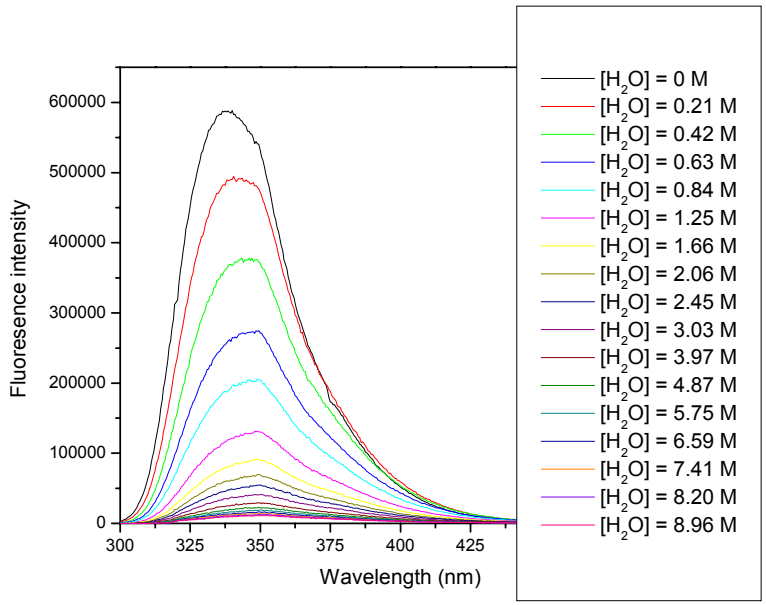
Excitation and emission spectrum of 3-(2'-hydroxyphenyl)pyridine (1b) in methanol



Fluorescence spectra of 3-(2'-hydroxyphenyl)pyridine (1b) in acetonitrile in the presence of different water concentrations (λ_{ex} = 290 nm)



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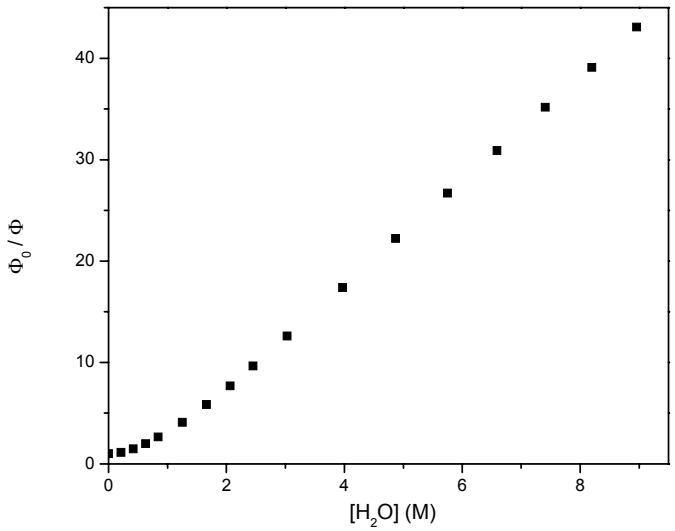
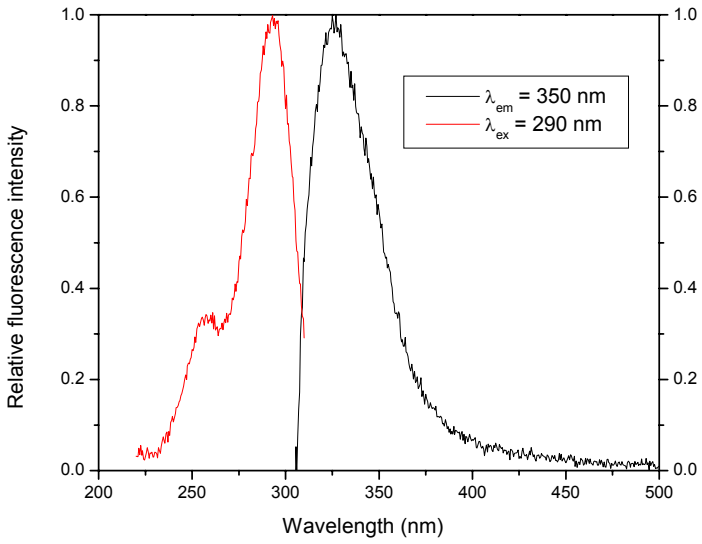
Stern-Volmer plot of the quenching of fluorescence of 3-(2'-hydroxyphenyl)pyridine (1b) in acetonitrile by water



Excitation and emission spectrum of 4-(2'-hydroxyphenyl)pyridine (1c) in cyclohexane



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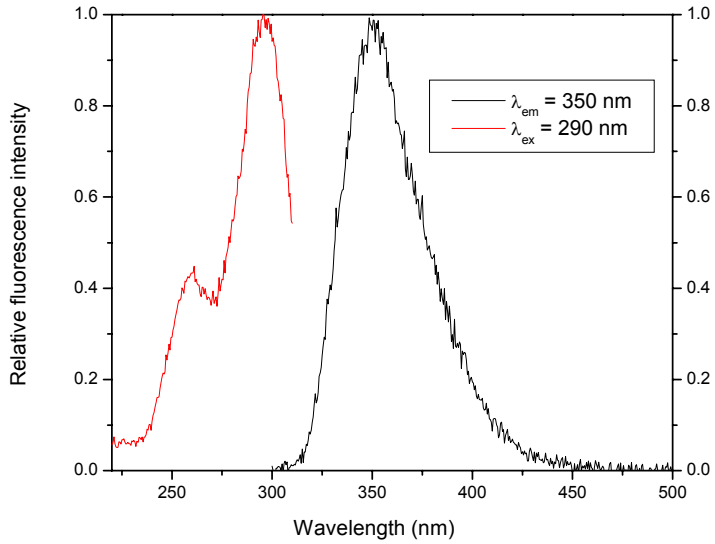
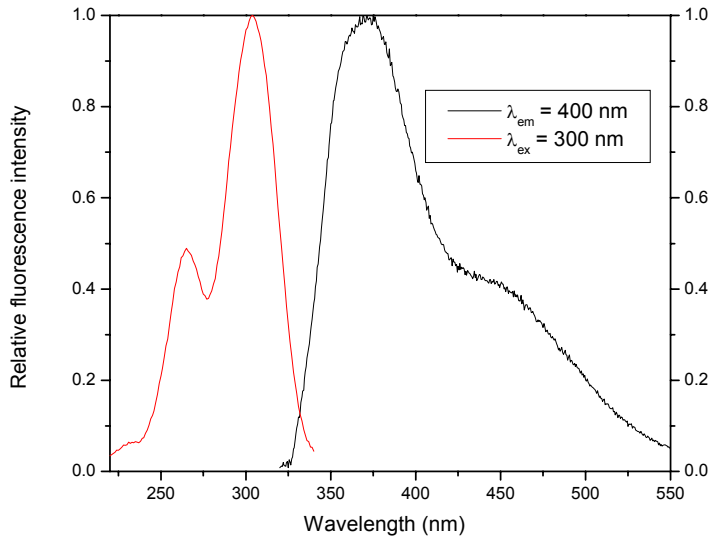
Excitation and emission spectra of 4-(2'-hydroxyphenyl)pyridine (1c) in acetonitrile (above) and methanol (bellow)





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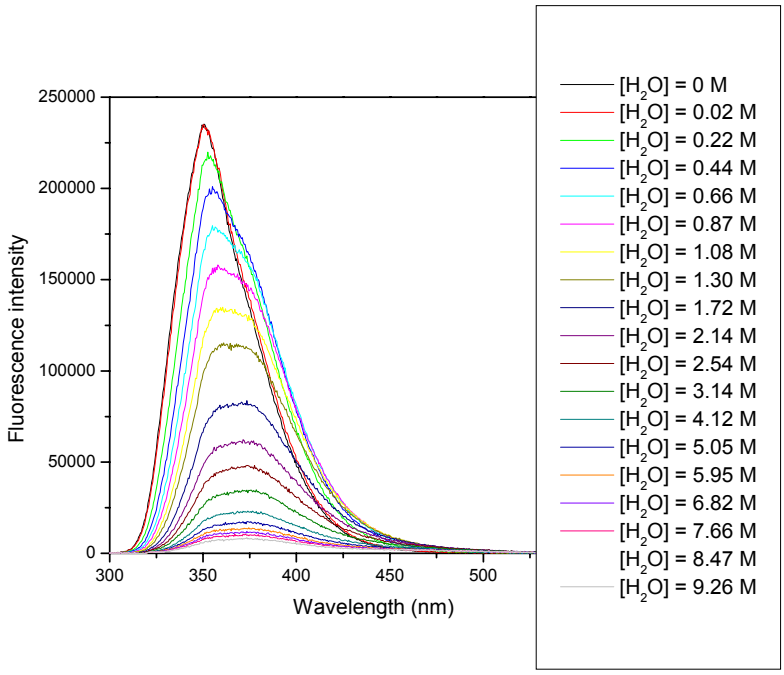
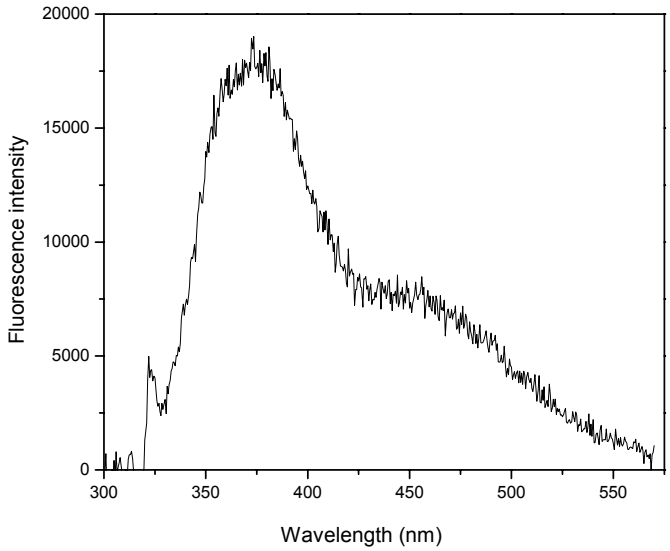
Fluorescence spectra of 4-(2'-hydroxyphenyl)pyridine (1c) in acetonitrile in the presence of different water concentrations (λ_{ex} = 290 nm)



Emission spectrum of 4-(2'-hydroxyphenyl)pyridine (1c) in acetonitrile in the presence of 12.8 M H_2O (λ_{ex} = 290 nm)



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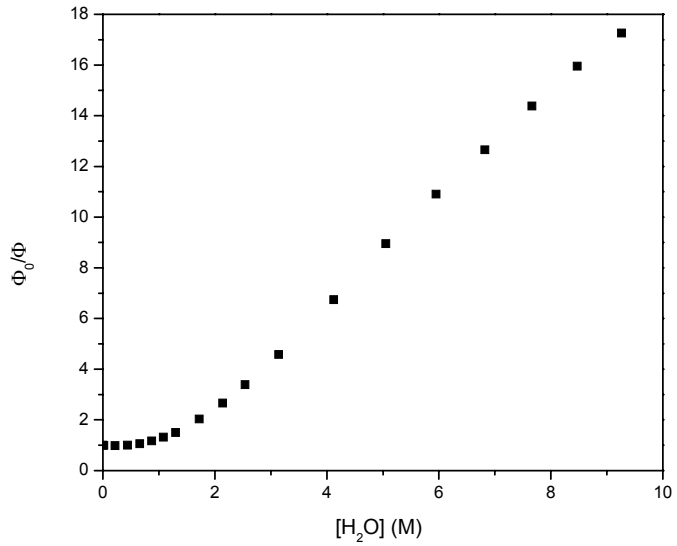
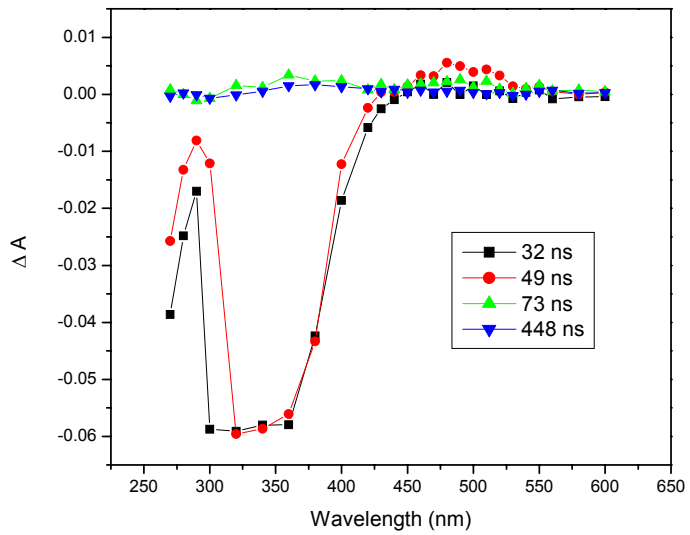
Stern-Volmer plot of the quenching of fluorescence of 4-(2'-hydroxyphenyl)pyridine (1c) in acetonitrile by water



Transient absorption spectra of 2-(2'-hydroxyphenyl)pyridine (1a) recorded in N_2 purged CH_3CN



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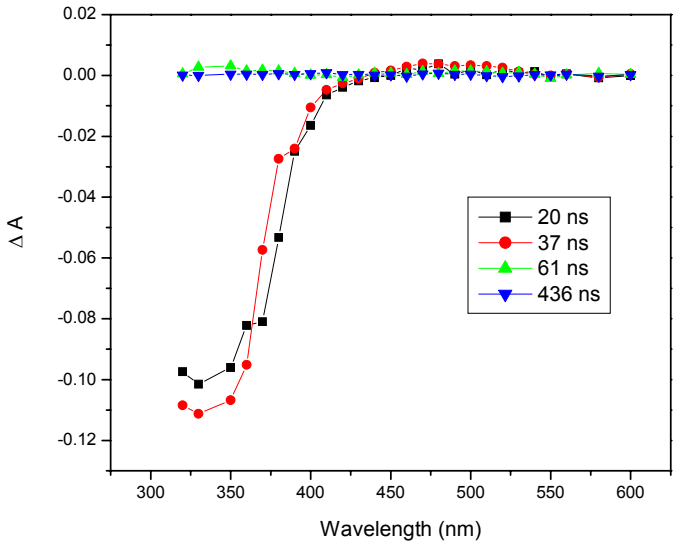
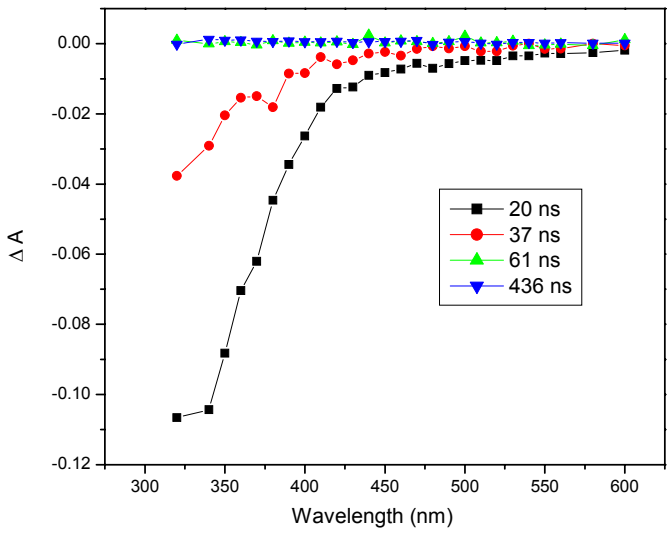
Transient absorption spectra of 2-(2'-hydroxyphenyl)pyridine (1a) recorded in O_2 purged CH_3CN



Transient absorption spectra of 2-(2'-hydroxyphenyl)pyridine (1a) recorded in N_2 purged CH_3CN:H_2O (1:1)



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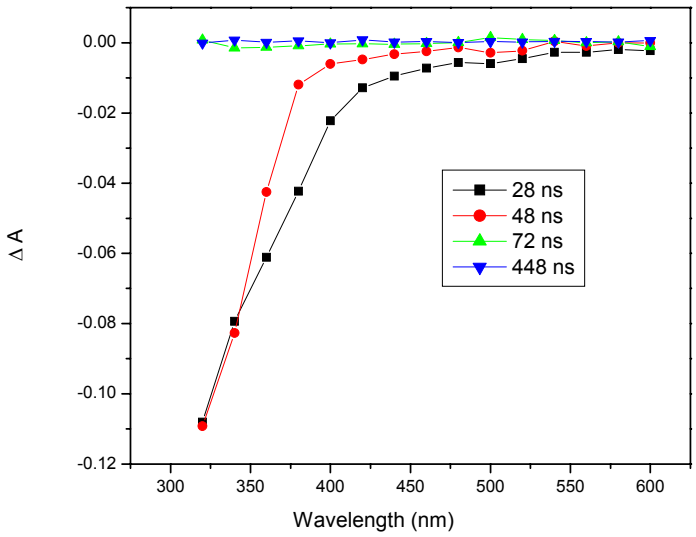
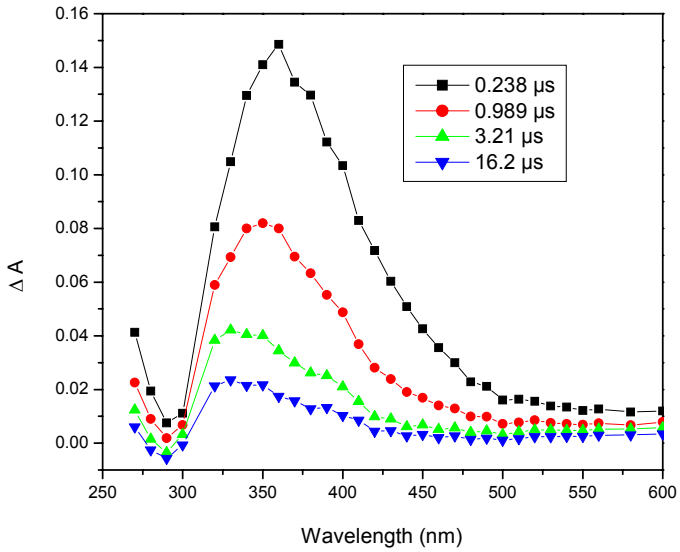
Transient absorption spectra of 2-(2'-hydroxyphenyl)pyridine (1a) recorded in O_2 purged $CH_3CN:H_2O$ (1:1)



Transient absorption spectra of 3-(2'-hydroxyphenyl)pyridine (1b) recorded in N_2 purged CH_3CN



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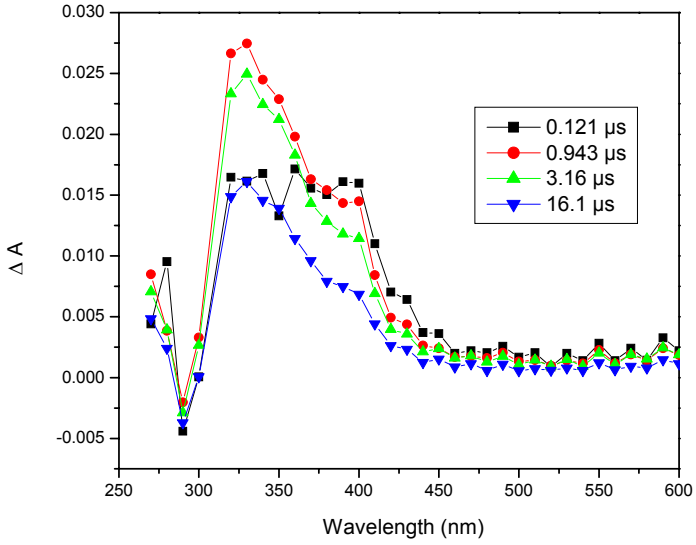
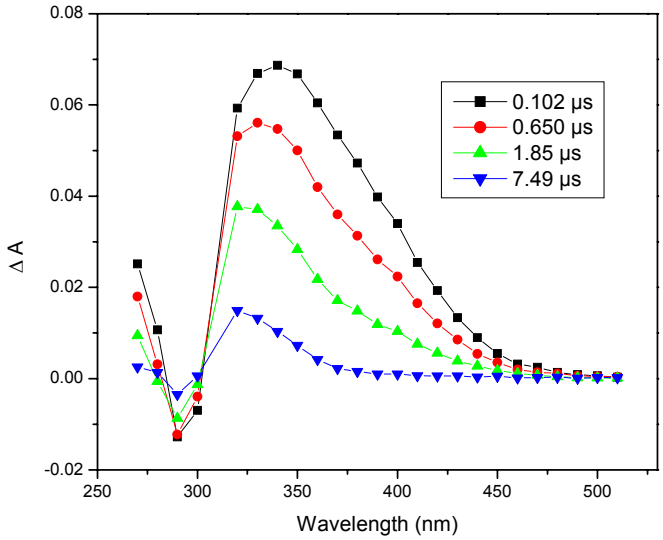
Transient absorption spectra of 3-(2'-hydroxyphenyl)pyridine (1b) recorded in O_2 purged CH_3CN



Transient absorption spectra of 3-(2'-hydroxyphenyl)pyridine (1b) recorded in N_2 purged CH_3CN:H_2O (1:1)



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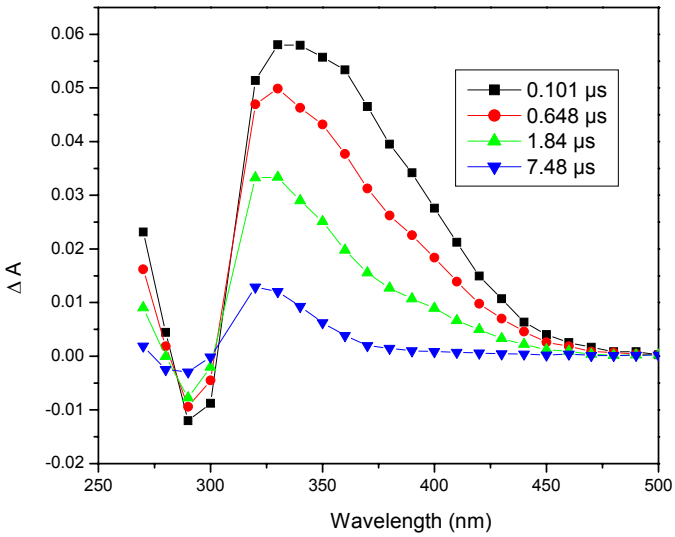
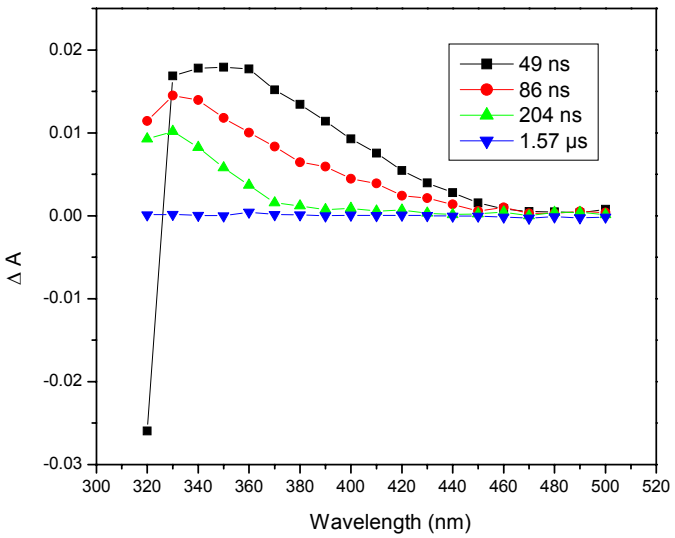
Transient absorption spectra of 3-(2'-hydroxyphenyl)pyridine (1b) recorded in O_2 purged $CH_3CN:H_2O$ (1:1)



Transient absorption spectra of 3-(2'-hydroxyphenyl)pyridine (1b) recorded in O_2 purged $CH_3CN:H_2O$ (1:1) in the presence of ethanolamine (0.01 M)



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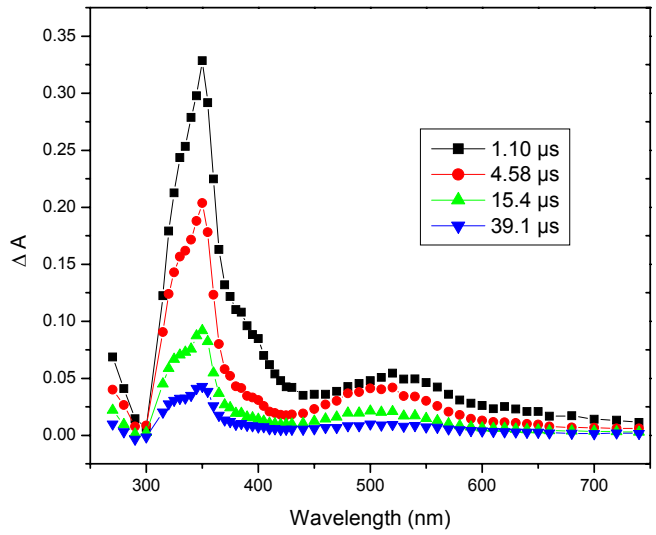
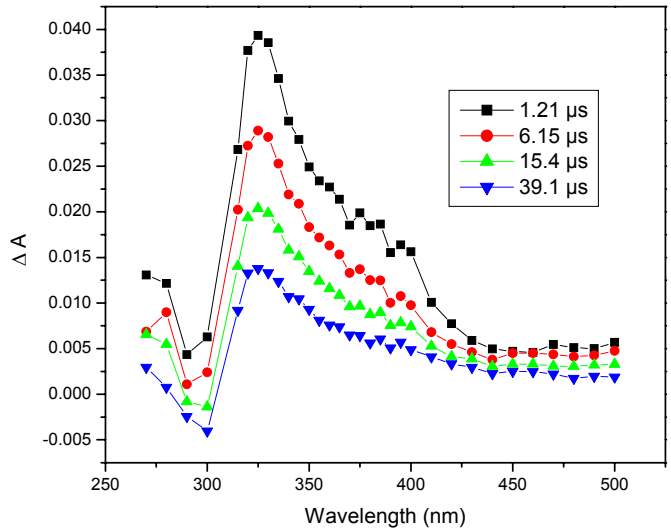
Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in N_2 purged CH_3CN



Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in O_2 purged CH_3CN



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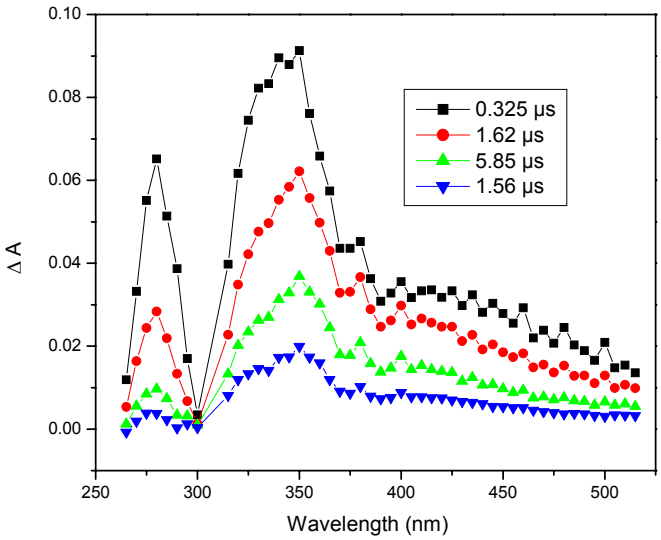
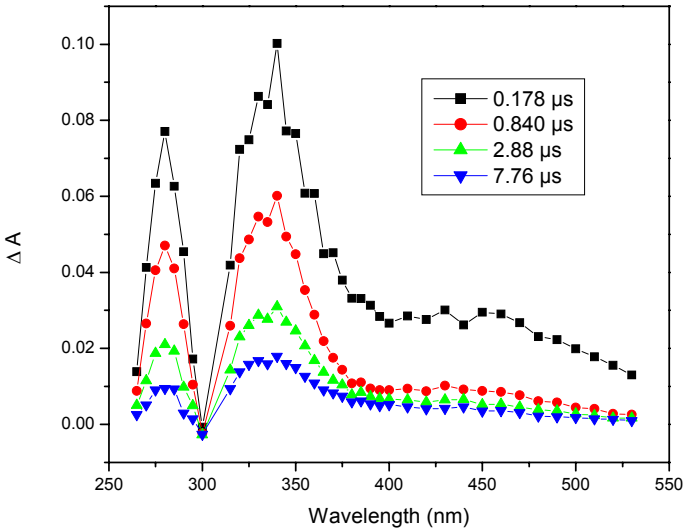
Transient absorption spectra of 4-(2'-methoxyphenyl)pyridine recorded in N_2 purged $CH_3CN:H_2O$ (1:1)



Transient absorption spectra of 4-(2'-methoxyphenyl)pyridine recorded in O_2 purged $CH_3CN:H_2O$ (1:1)



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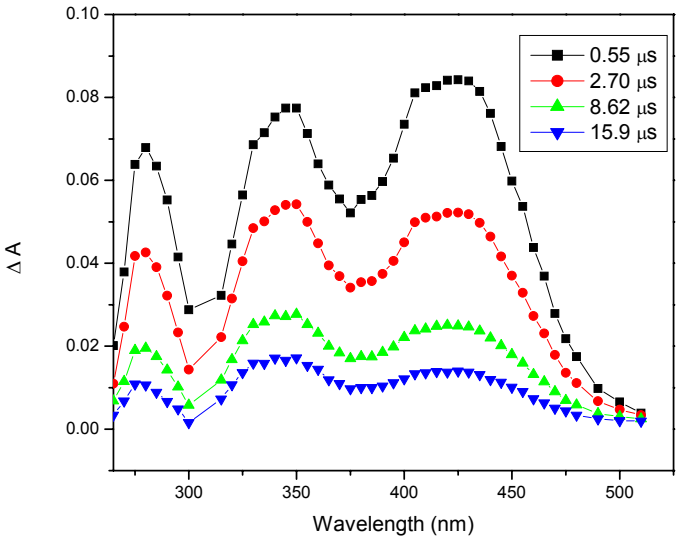
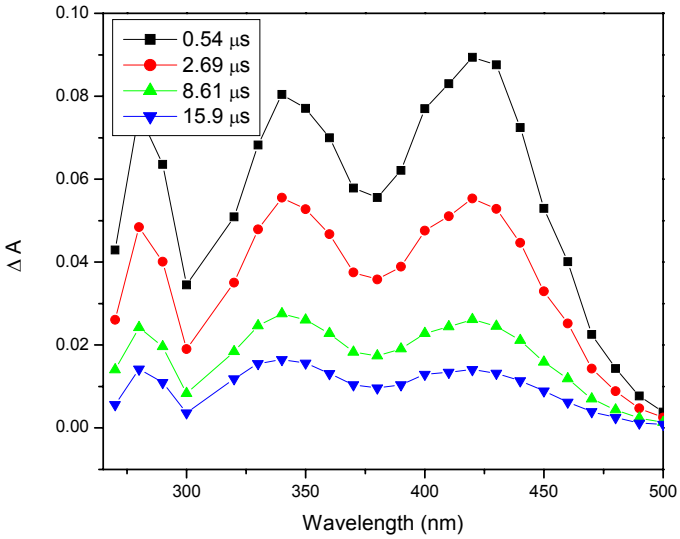
Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in N_2 purged $CH_3CN:H_2O$ (1:1)



Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in O_2 purged $CH_3CN:H_2O$ (1:1)



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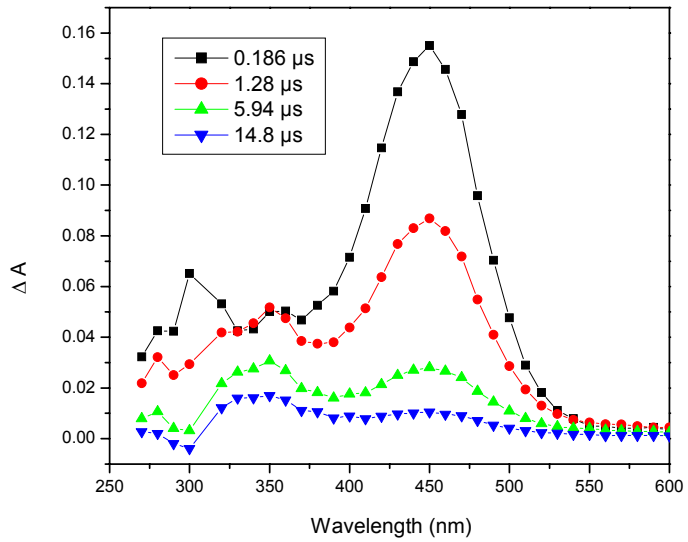
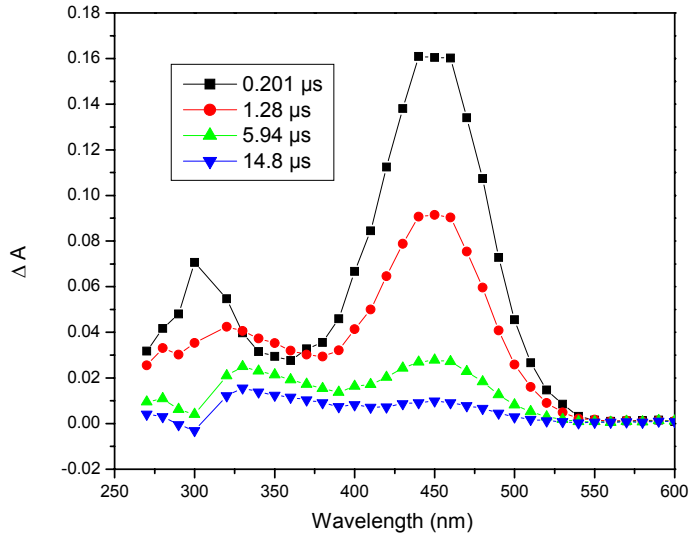
Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in N_2 purged $CH_3CN:H_2O$ (10 %)



Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in O_2 purged $CH_3CN:H_2O$ (10 %)



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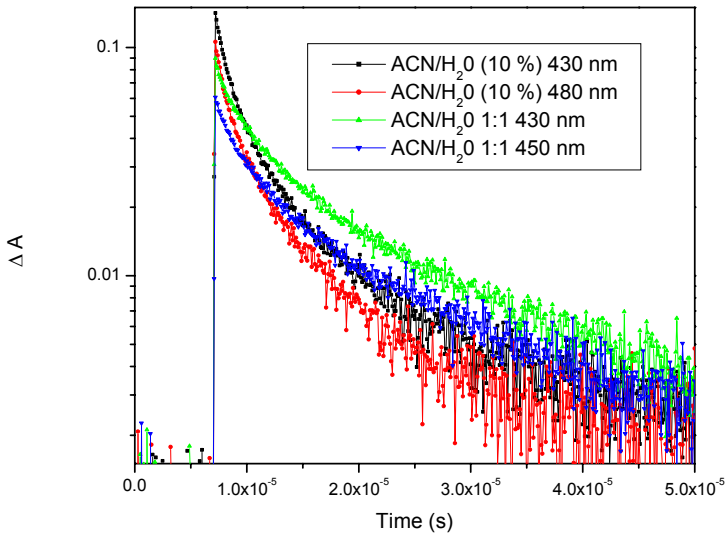
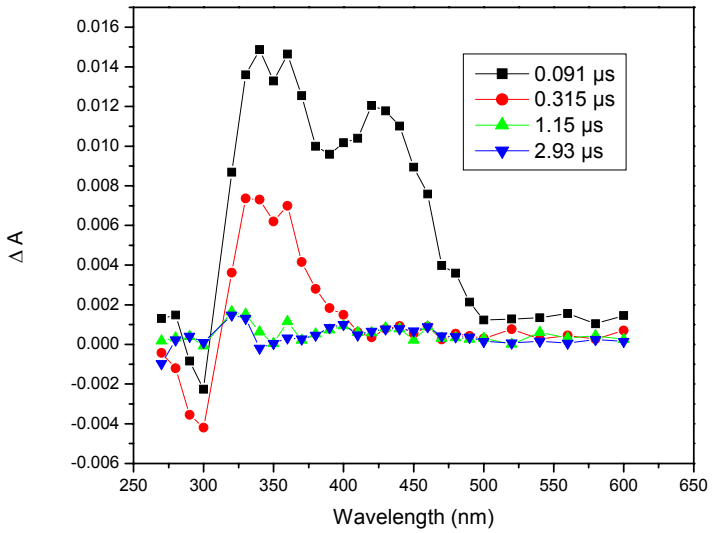
Decays of transient absorptions for 4-(2'-hydroxyphenyl)pyridine (1c), recorded in O_2 purged $CH_3CN:H_2O$



Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in O_2 purged $CH_3CN:H_2O$ (1:1) in the presence of ethanolamine (0.08 M)



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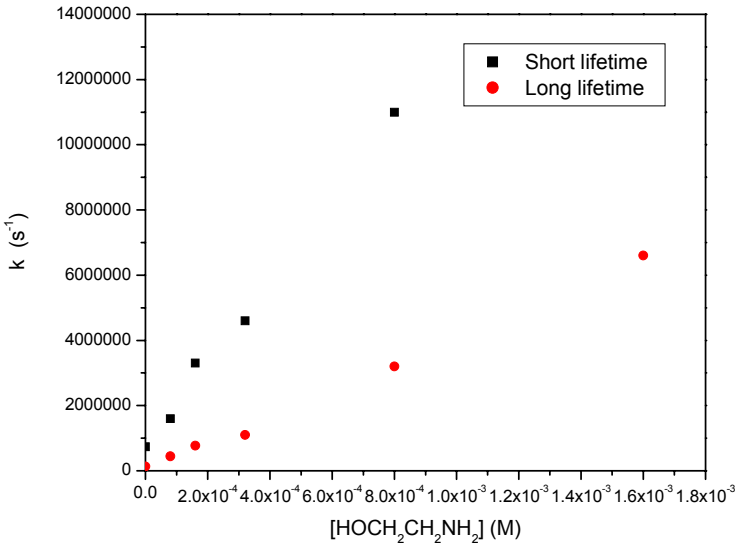
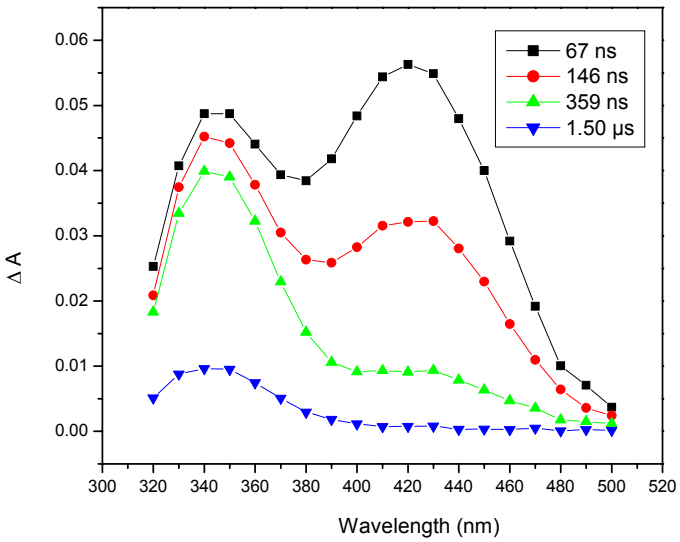
Dependence of the rate constants for the decay of transient absorption of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in O_2 purged $CH_3CN:H_2O$ (10 %) on the concentration of ethanolamine



Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in O_2 purged $CH_3CN:H_2O$ (1:1) in the presence of 5 mM phosphate buffer at pH 7



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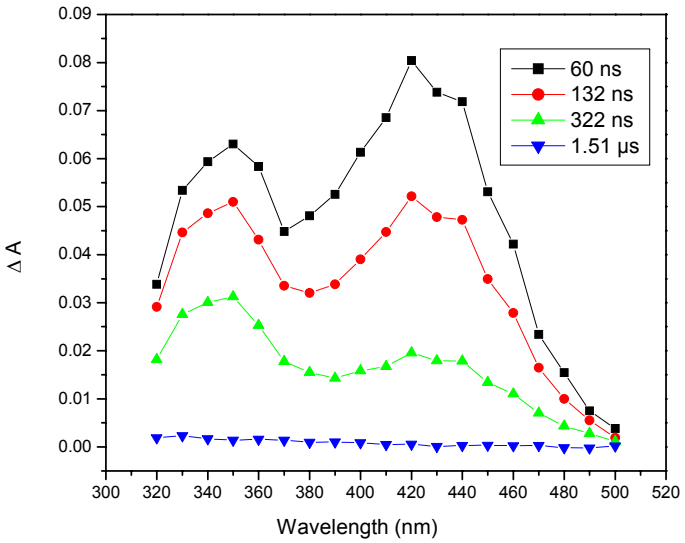
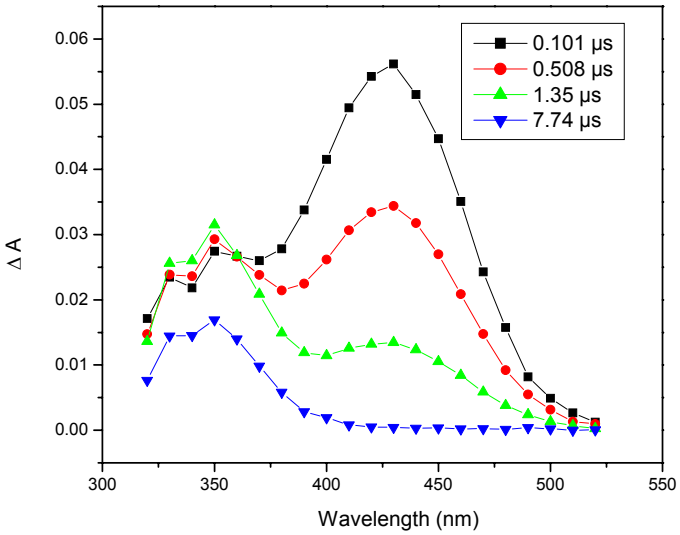
Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in O_2 purged $CH_3CN:H_2O$ (1:1) in the presence of 5 mM phosphate buffer at pH 6



Transient absorption spectra of 4-(2'-hydroxyphenyl)pyridine (1c) recorded in O_2 purged $CH_3CN:H_2O$ (1:1) in the presence of 5 mM borate buffer at pH 9



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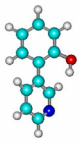
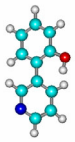
AM1 Heats of formation (Hyperchem)

The conformers of **1b**:

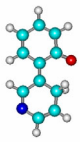


ΔH_f = 13.642 kcal / mol

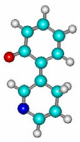


ΔH_f = 13.575 kcal / mol

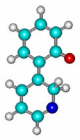
Two isomers of QM **14** and QM **15** (only isomers on the left probable)



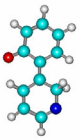
ΔH_f = 47.408 kcal/mol



ΔH_f = 49.362 kcal/mol

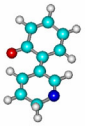


ΔH_f = 48.695 kcal/mol

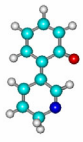


ΔH_f = 49.927 kcal/mol

Two isomers of QM **16**



ΔH_f = 51.008 kcal/mol



ΔH_f = 51.330 kcal/mol