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Photoinduced fluorescence changes on *E–Z* isomerisation in azobenzene derivatives

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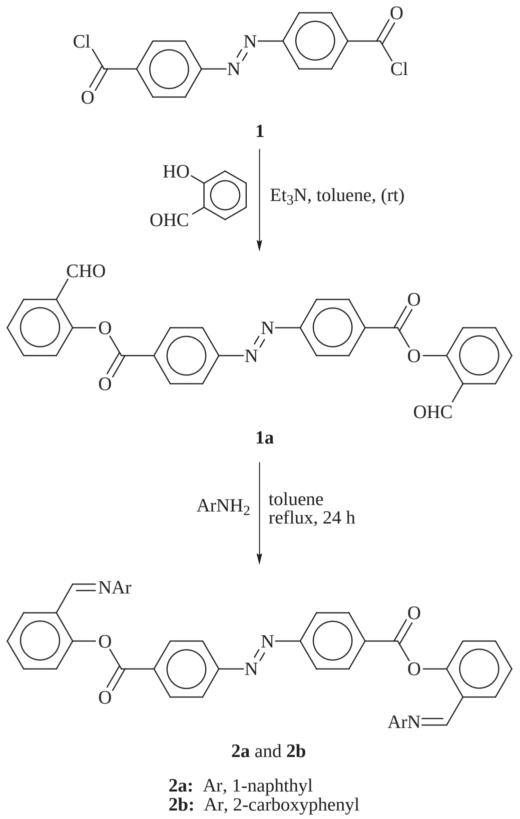
New fluorosensors based on azobenzene derivatives have been synthesised, characterised and their photophysical properties investigated. Compounds 2a and 2b undergo $E\rightarrow Z$ photoisomerisation on irradiation at ~330 nm accompanied by fluorescence enhancement. $Z\rightarrow E$ isomerisation in the dark is accompanied by a decrease in the fluorescence intensity. These are the first reported examples of fluorescence enhancement on $E\rightarrow Z$ isomerisation across a N=N bond. Protonation of the azo groups in 2a and 2b is also accompanied by fluorescence enhancement. The origin of the fluorescence enhancement in the *cis* isomer is explained on the basis of the inhibition of photoinduced electron transfer due to the nonplanar geometry of this isomer, which reduces the effective conjugation of the nitrogen lone pair electrons with the π electrons of the fluorophore.

Introduction

The design of molecular systems which change their physical and chemical properties in response to light is of interest because of a wide range of applications.[1] Azobenzene and its derivatives undergo conversion from the *trans* (*E*) form to the *cis* (*Z*) form on irradiation at 310 nm and revert to the (*E*) form on irradiation at 440 nm or in the dark. This photochemical change leads to a photostationary equilibrium (PSE).[2] Photoinduced changes of azobenzene have been monitored to study the change in the electric resistance due to $E\leftrightarrow Z$ isomerisation,[3] the change in the conformation of polypeptides,[4] change in the binding ability of β-cyclodextrin[5] and the change in the ion extractability of crown ethers.[6] Naphthalene outfitted with a crown ether binding site can monitor the association of alkaline earth metals from the changes in the naphthalene fluorescence.[7] Subsequently fluorescent chemosensors have been developed by several groups.[8–12]

Reversible *trans–cis* isomerisation of azobenzene derivatives generally does not induce a change in fluorescence since azo compounds do not emit.[13] However, on suitable coupling of fluorophores, such as 1-aminonaphthalene and 2-aminobenzoic acid to azobenzene systems, the *trans*↔*cis* isomerisation of the system induces changes in the fluorescence properties of the fluorophores. Here we wish to report for the first time the observation of such fluorescence changes in azobenzene systems due to *trans*↔*cis* isomerisation. The synthesis and characterisation of two such systems and photophysical changes in them on $E\leftrightarrow Z$ isomerisation are discussed.



Scheme 1

Results and discussion

The syntheses of the azobenzene fluorosensors **2a** and **2b** are shown in Scheme 1 and the details are given in the Experimental section. The products were purified by repeated recrystallisations from hot toluene and are confirmed to be analytically pure for photochemical studies. The characterisation data for compounds **2a** and **2b** suggest that aminolysis of the ester groups has not occurred during the Schiff base condensations.

UV–VIS absorption spectra

In azobenzene derivatives, $E\rightarrow Z$ isomerisation and the conversion efficiency depend largely on the nature of the substituents, the position of substitution on the azobenzene ring and the nature of the solvent. *cis* forms are stabilised more in polar solvents and hence the percentage of this isomer is greater in acetonitrile than in *o*-dichlorobenzene.[14]

The UV–VIS spectra of the compounds **2a** and **2b** are characterised by high intensity bands around 335 and 330 nm and low intensity bands around 455 and 460 nm respectively. The spectral changes accompanying photochemical conversion of $E\rightarrow Z$ form on irradiation of **2a** at 335 nm are shown in Fig. 1. A similar trend is observed in the case of **2b**. Data on the rate of photochemical generation of the *Z* forms, rate of thermal regeneration of the *E* forms, and the percentage compositions of both the forms at the photostationary state in *o*-dichlorobenzene are presented in Table 1. On $E\rightarrow Z$ isomerisation, the intense absorption band at ~335 nm decreases and the absorption maximum at 460 nm increases in unequal proportions. The extent of $E \rightarrow Z$ photochemical conversion is determined by measuring the change in ε values of the ~335 nm band at 15 minute intervals during irradiation. The 460 nm bands are in slightly different positions for each compound, whereas the ~335 nm bands are unaffected by the nature of the substitution on the azobenzene rings.

The absorption band at ~335 nm is related to the $\pi \rightarrow \pi^*$ transition of the N=N unit. The *E* form is more stable and the percentage of the *Z* form is negligible compared to that of the *E* form under normal conditions. The weak absorption band at *ca.* 460 nm is the low energy $n \rightarrow \pi^*$ transition of the N=N unit. The photoisomerisation of *E* to *Z* in compounds **2a** and **2b** follows first order kinetics. $Z \rightarrow E$ isomerisation in the dark also follows first order kinetics. More than 90% of the *cis* form re-isomerised to the *trans* form after 360 h in the dark. In another set of experiments, re-isomerisations of the samples **2a** and **2b** were carried out photochemically by irradiation at 460 nm. This yielded 99% conversion to the *trans* isomer after 4 h.

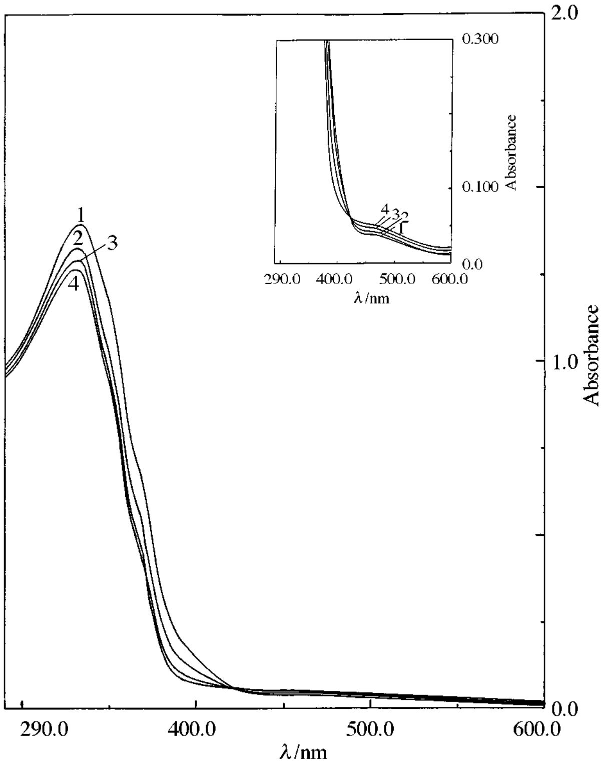


Fig. 1 UV–VIS spectra of **2a** and the changes accompanying photochemical conversion of $E \rightarrow Z$ form on irradiation at 335 nm as a function of time; (1) before irradiation; (2) irradiation time 15 min; (3) 30 min; (4) 115 min. *Inset*, increase in the intensity of $n \rightarrow \pi^*$ band as a function of irradiation time.

Fluorescence emission spectra

The high intensity band at ~330 nm of the UV–VIS spectra was excited and monomer-like emissions were observed at ~406 nm for **2a** and at 400 nm for **2b**. The position of λ_{Em} (emission wavelength) showed minor deviations depending on the nature of the fluorophore. Emission profiles as a function of irradiation time for molecule **2a** are shown in Fig. 2. Emission spectra as a function of time in the dark for molecule **2a** are shown in Fig. 3. Emission profiles of **2b** also show similar trends. Emission spectral data of **2a** and **2b** in *o*-dichlorobenzene are given in Table 1. Reference compounds **3a**–**3d** do not show fluorescence emission enhancement on irradiation at ~330 nm. Fluorescence excitation spectra have been measured for molecules **2a** and **2b** and they are similar to the UV–VIS absorption spectra in the region 300–385 nm.

These results show that on irradiation, the emission of both **2a** and **2b** is enhanced. Generally azo compounds do not emit even under conditions that normally promote such behaviour such as deuteration, incorporation in a vitreous matrix, incorporation in solid solution, low temperatures, *etc.* While the emission observed in **2a** and **2b** originates from the fluorophores that are coupled to azobenzene, the enhanced emission of **2a** and **2b** on excitation results from the $E \rightarrow Z$ isomerisation already characterised in these systems (*vide supra*). For the molecule **2a**, the emission was enhanced by 13-fold at the photostationary equilibrium (PSE). For **2b**, the emission was enhanced by 6-fold of the non-irradiated starting solution at the PSE. There is no further enhancement in emission after the photostationary equilibrium is reached. $Z \rightarrow E$ isomerisation in the dark was followed by a decrease in the emission intensity. After 360 h in the dark, the emission intensity of **2a** was found to decrease to 3-fold from 13-fold at the photostationary state. In other words, ~75% $Z \rightarrow E$ conversion had taken place. In the case of **2b**, the emission intensity decreased to 2-fold from 6-fold at the photostationary state and the percentage of conversion was found to be ~60%.

Additional support for the photo enhanced fluorescence (PEF) of **2a** and **2b** on $E \rightarrow Z$ photoisomerisation comes from the following experiments. Molecules **3a** and **3b**, structurally

Table 1 UV–VIS and emission spectral data of molecules **2a**, **2b** and **3a**–**3d** in *o*-dichlorobenzene

	$E \rightarrow Z$ (*hv*; 335 nm)			$Z \rightarrow E$ (dark)		
UV–VIS[a]	λ (ε_1)	λ (ε_2)	$Z:E$ (%)	λ (ε_3)	$k^{-1}/10^8$ s^{-1}	$Z:E$ (%)
2a	455 (630) 335 (34 790)	449 (1290) 335 (30 050)	14:86	453 (968) 335 (33 050)	6.59	5:95
2b	460 (750) 330 (40 940)	460 (890) 330 (29 770)	27:73	460 (780) 330 (38 500)	7.84	6:94
Emission[b]	φ_{f1}	φ_{f2}	E.F.	φ_{f3}	t_2/h	Q.F.
2a	0.008	0.104	13	0.026	360	4
2b	0.110	0.690	6.3	0.266	360	2.6
3a	0.001	0.001	1.0			
3b	0.390	0.355	*c*			
3c	0.110	0.115	1.05			
3d	0.430	0.408	*c*			

[a] λ/nm; Molar extinction coefficients (ε/dm^3 mol^{-1} cm^{-1}); ε_1, before irradiation; ε_2, after irradiation at 335 nm or 330 nm in **2a** and **2b** respectively, *viz.*, at the photostationary state, reached after 115 min in **2a** and after 90 min in **2b**; ε_3, at the stage of maximum $Z \rightarrow E$ conversion in the dark after 216 and 360 h respectively; k^{-1}, rate constant for the $Z \rightarrow E$ conversion in the dark at 27 °C. [b] φ_{f1}, Quantum efficiency before irradiation; φ_{f2}, quantum efficiency at the photostationary state; φ_{f3}, quantum efficiency at the stage of maximum $Z \rightarrow E$ conversion in the dark; calculated using quinine sulfate as a standard; t_2, time required for maximum $Z \rightarrow E$ conversion in the dark; E.F., enhancement factor; Q.F., quenching factor. [c] Cannot be calculated as the intensity decreased on irradiation.

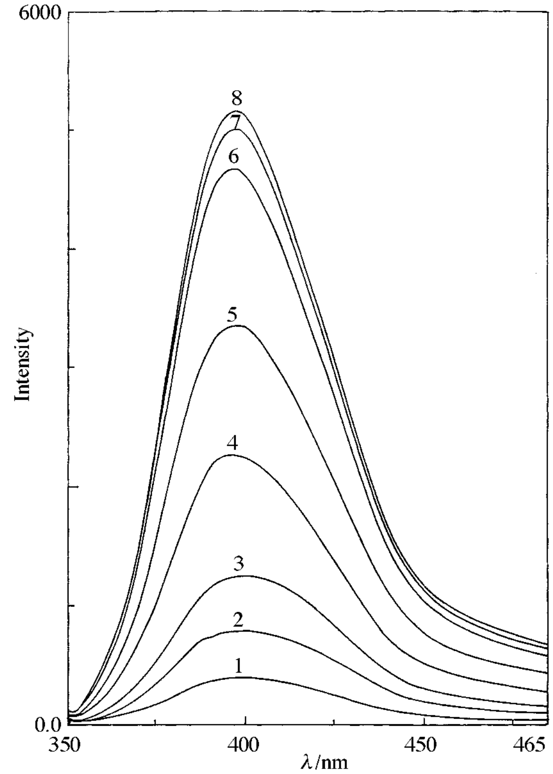


Fig. 2 Corrected emission spectra of **2a** as a function of irradiation time for forward $E \rightarrow Z$ process; (1) before irradiation; (2) irradiation time 5 min; (3) 15 min; (4) 30 min; (5) 45 min; (6) 60 min; (7) 75 min; (8) 115 min

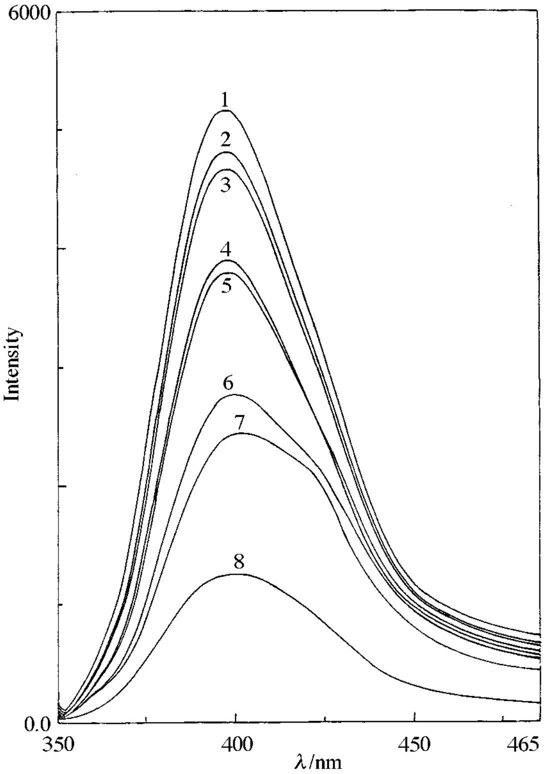
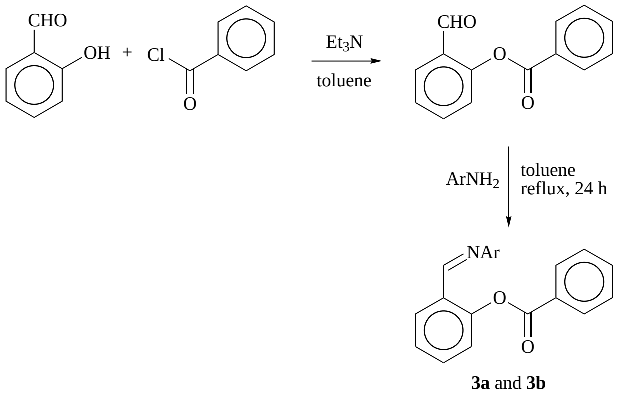


Fig. 3 Corrected emission spectra of **2a** as a function of time for backward $Z \rightarrow E$ process in the dark; (1) at the photostationary state; (2) after 4 h in the dark; (3) after 8 h; (4) after 20 h; (5) after 96 h; (6) after 120 h; (7) after 180 h; (8) after 360 h

analogous but without the N=N unit were synthesised as shown in Scheme 2 and the emission spectra were monitored under similar conditions as a function of irradiation time at 330 nm. The emission spectra over a period of 60 min showed only a marginal increase in intensity in **3a** and a marginal decrease in **3b**. Similarly the fluorophores, pure 1-aminonaphthalene (**3c**) and *o*-aminobenzoic acid (**3d**) were irradiated at ~330 nm, and the emission spectra were recorded as a function of irradiation time. In this case too the emission spectra over a period of 60 min showed only a marginal increase in intensity in **3c** and a marginal decrease in **3d**. Therefore the enhancement of fluorescence emission in **2a** and **2b** is due to $E \rightarrow Z$ isomerisation with respect to the –N=N– bond and not due to isomerisation across the –CH=N– bond.[15]



3a and **3b**

3a: Ar, 1-naphthyl
3b: Ar, 2-carboxyphenyl

Scheme 2

The fluorescence enhancement upon *cis* isomerisation could be due to inhibition of the photoinduced electron transfer (PET) mechanism.[16] The *cis* isomer formed on irradiation is non planar and therefore the lone pair electrons on nitrogen can no longer effectively conjugate with the π-electrons of the fluorophore, thereby inhibiting the PET mechanism. MO theory predicts C_{2h} and C_{2v} symmetry for the n-orbitals of the *trans* and *cis* isomers respectively.[13] The inhibition of PET increases the φ_f value of the system (*cis* isomer) to 0.104 from the value of 0.008 (*trans* isomer).

Effect of protonation on emission spectra

Operation of the PET phenomenon has been checked by protonation experiments. Titration of **2a** and **2b** with H_2SO_4 (~0.1 M) in DMF leads to the loss of the n→π* band at 460 nm in the UV–VIS spectra whereas the π→π* band remained unaffected. In contrast, fluorescence was enhanced by 3-fold in **2a** and 2.5-fold in **2b** (λ_{Ex}, 335 nm; λ_{Em}, 416 nm) at low concentration of protons (pH, 1.43) in DMF due to some protonation of the –N=N– bond.[17] In the protonated form, the lone pair electrons are not available for quenching the fluorescence of fluorophores (electron acceptors) by the electron transfer (PET) mechanism and hence enhanced emission can be observed.[16,18] The enhanced emission follows the order **2b** > **2a**. The protonation of azo nitrogens also results in the loss of the n→π* band at 455 nm in the UV–VIS spectrum. It may be noted that reference compound **3a** with the fluorophore group but without the azo group did not exhibit any fluorescence enhancement in a similar protonation experiment. This shows that protonation of the –C=N– group although possible under the experimental conditions does not enhance the fluorescence. Higher concentration of protons can lead to the hydrolysis of ester groups accompanied by decreased emission intensities by about 2.5-fold in both the cases. This is confirmed by the hydrolysis of **2a** and **2b** which gives the non-fluorescent methyl ester compound in methanol.

In coordinating solvents the φ_f value of the *trans* form of **2a** increases to 0.045 in DMF and 0.036 in MeCN, whereas it is 0.008 in *o*-dichlorobenzene. Proton transfer from the –COOH group in **2b** to –N=N– is also not expected on irradiation and cleavage of the –CH=N– bond is insignificant because of the reversibility of the process. The UV–VIS absorption, emission and ^{1}H NMR spectra remained similar without any visible changes before and after irradiation except minor changes in the intensities.

Excited state life time measurements of **2a** before irradiation show the presence of two kinetically distinguishable species of different amplitudes (96 and 4%) with life times (Tf) 2 and 5 ns and are assigned to *trans* and *cis* isomers. On irradiation for 1 h only the relative amplitudes changed (74.5 and 25.5%) with Tf values of 1.9 and 4.6 ns. The *cis* isomer of **2a** has a longer life time. The Tf values of the reference compounds **3a** and **3c** remain unaffected by irradiation. These results are in agreement with the UV–VIS spectral results.

Conclusion

These results demonstrate that *E*–*Z* isomerisation across the −N=N− bond in azobenzene derivatives outfitted with suitable fluorophores can be monitored by fluorescence spectral changes. The isomerisation process is found to be reversible. The fluorescence enhancement is attributed to the inhibition of PET in the *cis* isomer. Protonation of the N=N bond results in enhancement of fluorescence emission supporting the operation of the PET mechanism.

Experimental

General

The elemental analysis was carried out on a Perkin-Elmer 240C elemental analyser. FTIR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer in the range 4000–600 cm^{-1} as KBr pellets. ^{1}H NMR spectra were recorded on a Bruker MSL-500 NMR spectrometer in $CDCl_3$ using TMS (tetramethylsilane) as an internal standard. Electronic spectra were recorded on a JASCO model 7800 UV–VIS spectrophotometer using ~0.25 × 10^{-4} M solutions in distilled *o*-dichlorobenzene. Fluorescence experiments were carried out in distilled *o*-dichlorobenzene and *N*,*N*-dimethylformamide (DMF) on a JASCO model FP-777 spectrofluorometer at room temperature. All the solvents were distilled and dried.

Photoisomerisation and kinetic measurements

Photoisomerisation of *E* to *Z* form was carried out in *o*-dichlorobenzene with a 150 W xenon short arc lamp provided with a f/4 monochromator. The distance from the source was maintained at 45 cm. The absorbance was recorded at room temperature in the range 600–275 nm in *o*-dichlorobenzene. Subsequently the samples were irradiated at ~330 or ~335 nm and the absorbance of the band was monitored as a function of time. Irradiation was discontinued when the photostationary equilibrium (PSE) was reached (when no further change in ε values of the band occurred). When the PSE was reached, the sample was quickly transferred to a standard measuring flask and kept in the dark to carry out the kinetic measurements. The absorbance of the band at 335 nm was recorded as a function of time in the dark. The percentage compositions of *Z* and *E* isomers were calculated on the assumption that the *E* isomer is 100% before irradiation.[6]

Fluorescence experiments

The concentrations of the samples were maintained at ~0.25 × 10^{-4} M. The fluorescence spectra were recorded before irradiation and subsequently the samples were irradiated at ~330 or 335 nm and fluorescence emission at ~400 nm was recorded as a function of time. Both emission and excitation slit band widths were 5 nm in all the cases. After the attainment of PSE, irradiation was discontinued and the fluorescence spectra for the backward *Z*→*E* reactions were recorded as a function of time in the dark. Quantum yields were calculated by the comparison of the areas under the curves of isooptical density solutions of samples and quinine sulfate (~1 × 10^{-4} M concentration in 2 M H_2SO_4). The effect of concentration of protons on the emission spectra was studied by adding different concentrations of ~0.1 M H_2SO_4 to isooptical density solutions of **2a** and **2b** (optical density was 0.6 at $\lambda = 330$ nm). 1-Aminonaphthalene, 2-aminobenzoic acid and 4-nitrobenzoic acid were recrystallised prior to use.

Excited state life time measurements

Excited state life time measurements were done on an IBH 5000 obtained from IBH consultants (UK). The source was a H_2 discharge coaxial nanosecond flash lamp with a pulse width of 1.4 ns and the photomultiplier was a Hamamatsu 3235. One thousand counts were employed in all the cases. The fluorescence decay of all the samples studied were fitted to biexponential decay function which yielded better χ^2 values (1.435). Deconvolution was carried out by the method of iterative reconvolution of the instrument response function and the assumed decay function. The goodness of the fit of the experimental data to the assumed decay function was judged by the standard statistical tests, *i.e.* random distribution of weighted residuals, the auto correlation function and the values of reduced χ^2. It is believed that the estimate on the error limit on the relative amplitudes should be less than 2–3%.

Syntheses of 2a and 2b

Compound **1a** was synthesised as described earlier.[14] Compound **1a** (1 mmol) in toluene (30 cm^3) was heated under reflux with 1-aminonaphthalene or 2-aminobenzoic acid (2 mmol) in toluene (30 cm^3) under N_2 for 24 h. The hot solution was filtered and the volume of the filtrate was reduced to give orange powders **2a** and **2b**. They were recrystallized from toluene. **2a**, 84%; mp 110–115 °C; ν_{max}/cm^{-1} 1732 (COO), 1624 (CH=N) and 1600 (N=N); δ_H(200 MHz; $CDCl_3$; 25 °C) 8.7 (s, 2H, CH=N), 8.4 (d, 4H, Ar), 8.3 (d, 4H, Ar), 8.1 (d, 4H, Ar), 7.8 (d, 4H, Ar), 7.7 (t, 4H, Ar), 7.3–7.6 (m, 10H, Ar), 6.9 (d, 2H, Ar); Calc. (Found) (%) C, 79.1 (79.0); H, 4.4 (4.6); N, 7.7 (7.8). **2b**, 72%, mp 134–136 °C; ν/cm^{-1} 1738 (COO), 1697 (COOH), 1620 (CH=N) and 1602 (N=N); δ_H(200 MHz; $CDCl_3$; 25 °C) 8.7 (s, 2H, CH=N), 8.4 (d, 4H, Ar), 8.2 (d, 4H, Ar), 8.0 (d, 2H, Ar), 7.75 (t, 2H, Ar), 7.50 (t, 2H, Ar), 7.35 (d, 2H, Ar), 7.0 (t, 2H, Ar), 6.7 (m, 6H, Ar); Calc. (Found) (%) C, 70.4 (70.2); H, 3.9 (4.0); N, 7.8 (8.0).

Syntheses of 3a and 3b

Salicylaldehyde (1 mmol) was stirred with 1 cm^3 of triethylamine in 60 cm^3 toluene under N_2 at room temperature for 30 min. Then 1 mmol of benzoyl chloride in 60 cm^3 of toluene was added dropwise under N_2 and stirred for 24 h at room temperature. The white precipitate of triethylamine hydrochloride was filtered off and the volume of the filtrate was reduced to give a light yellow oil. This compound (1 mmol) in 60 cm^3 toluene was heated under reflux with 1 mmol of 1-aminonaphthalene or 2-aminobenzoic acid for 24 h and cooled. Evaporation of toluene gave yellow semi-crystalline compounds, which were washed with hexane to give **3a** and **3b**. The syntheses of **3a** and **3b** are shown in Scheme 2. **3a**, 66%, ν_{max}/cm^{-1} 1741 (COO) and 1640 (CH=N); δ_H(200 MHz; $CDCl_3$; 25 °C) 8.6 (s, 1H, CH=N), 8.2 (d, 3H, Ar), 8.0 (d, 1H, Ar), 7.8 (m, 4H, Ar), 7.3–7.6 (m, 7H, Ar), 6.9 (d, 1H, Ar); Calc. (Found) (%) C, 82.0 (82.8); H, 4.8 (4.9); N, 3.9 (3.8). **3b**, 63%; ν/cm^{-1} 1741 (COO), 1700 (COOH) and 1640 (CH=N); δ_H(200 MHz; $CDCl_3$; 25 °C) 8.8 (s, 1H, CH=N), 8.2 (d, 3H, Ar), 8.0 (d, 1H, Ar), 7.5 (m, 5H, Ar), 6.7 (m, 4H, Ar); Calc. (Found) (%) C, 73.0 (72.8); H, 4.3 (4.2); N, 4.0 (3.8).

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