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## Supramolecular Chemistry

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### Epoxy-based polymer bearing activated azo dye (methyl orange) units: novel colorimetric indicator for amines

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## Epoxy-based polymer bearing activated azo dye (methyl orange) units: novel colorimetric indicator for amines

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Novel epoxy-based polymer **2**-bearing activated azo dye, 4-(4-sulphophenylazo)-*N,N*-dimethylaniline (methyl orange), moieties were synthesised by post-azo-coupling reaction of poly(hydroxy ether amine) **1** and investigated sensory responses towards amines. The reversible protonation–deprotonation chemistry of activated azobenzene moiety makes it of potential use as a colorimetric indicator for amines.

**Keywords:** epoxy-based azo polymer; indicator; amines

### Introduction

The rational design and synthesis of colorimetric indicators for amines, the important component of volatile organic compounds (VOCs), is currently of significant importance because of their toxic impacts on our environments (1–4). Accordingly, many molecular systems are being developed to recognise such environmentally important species (2, 5–7). Of particular interest is the development of polymeric indicating materials for amines exhibiting excellent stability and potential for reuse. However, epoxy-based polymers are more interesting because of their attractive properties such as easy processability, good chemical resistance and dimensional stability, and potential for reuse. Furthermore, azobenzene with electron-donating and electron-withdrawing groups at 4- and 4'-positions and hence is also described as 'push–pull-type' azobenzene provides versatile-responsive system. In this regard, the ability to construct epoxy-based azopolymer to yield better understanding of responsive effect of azobenzene moieties in the macromolecular structure still remains a significant challenge. To address this issue, this communication focuses on post-azo-coupling strategy to produce novel epoxy-based azo polymer **2**, in which the reversible protonation–deprotonation chemistry of 'push–pull-type' azobenzene moieties has been utilised in the colorimetric detection of amines. This is believed to be the first time that epoxy-based polymer with activated azo dye is made of and used as colorimetric indicator for amines.

### Results and discussion

#### Synthesis and characterisation

Epoxy-based precursor polymer [poly(hydroxy ether amine)] **1** was prepared by the reaction between diglycidyl ether

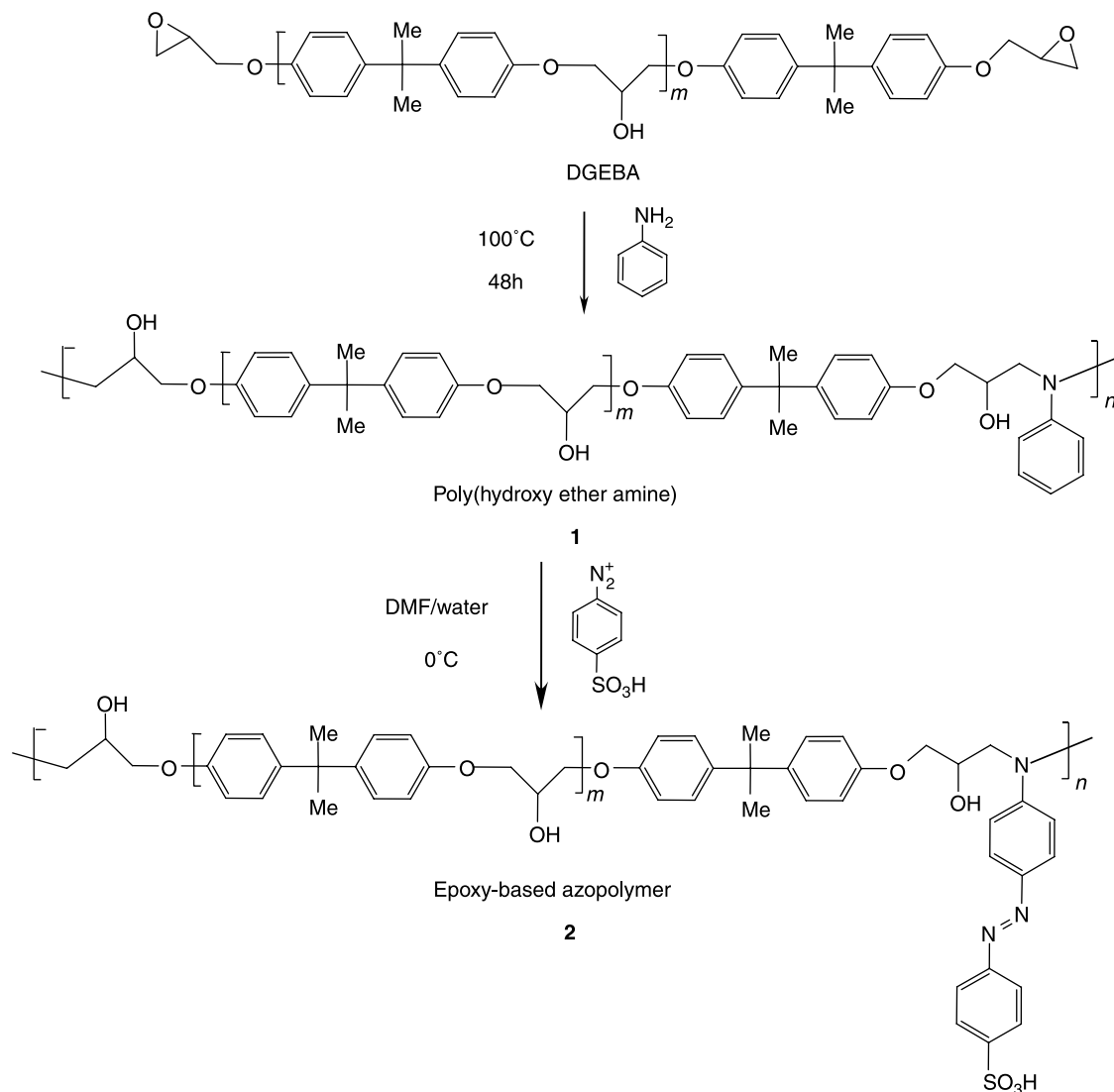
of bisphenol-A (DGEBA) and aniline following the reported procedure (8). Polymer **2** was then synthesised by applying post-azo-coupling reaction of **1** with benzene diazonium salt derived from 4-aminobenzene sulphonic acid (Scheme 1) and unambiguously characterised by FT-IR, UV–vis and NMR (<sup>1</sup>H and <sup>13</sup>C) analyses.

Diazonium salt readily attacks the benzene ring of aniline residue at positions with high electron densities. The resulting steric hindrance controls the aromatic electrophilic substitution to take place exclusively at the *para* position as evidenced from <sup>1</sup>H NMR analysis. Azo-coupling reaction of **1** resulted in a dramatic decrease in the resonance at 6.54 ppm assignable to the protons in the *p*-positions of aniline moieties. Further, the resonance attributed to protons *ortho* and *meta* to the aniline moieties shifted to lower magnetic field reflective of the introduction of electron-withdrawing azobenzene units. The degree of functionalisation (DF) was determined from the peak areas for the proton *para* to the free aniline moieties and the peak area at 1.55 ppm singlet that corresponds to the methyl protons of bisphenol-A moieties. The DF of **2** was estimated to be about 36% from the <sup>1</sup>H NMR analysis.

#### UV–vis spectral study

The strategy for the design of epoxy-based colorimetric indicating polymer is based on two ideas. First, significant stability of the macromolecular structure and the hydrolytic stability of methyl orange moiety under acidic/basic media. Second, the 'push–pull-type' azobenzene (methyl orange) moiety would activate the azo group to exhibit proton-induced colorimetric response. It is well established that in acidic media, the protonation of dye molecule occurs favourably at the azo group to create

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Scheme 1. Synthetic scheme of epoxy-based azopolymer **2**.

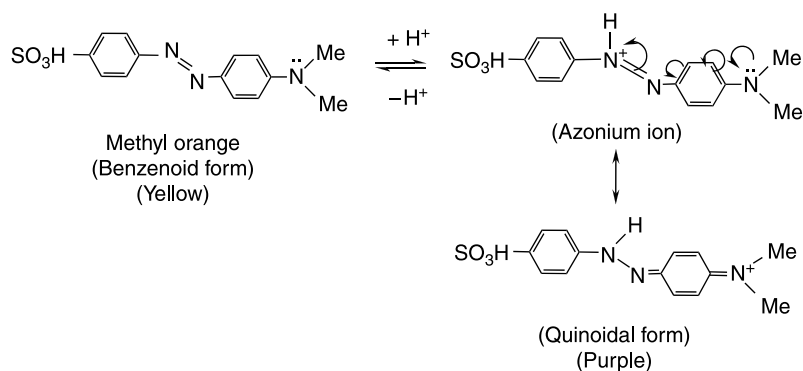
an azonium ion as the predominant species (9–11) with consequent colorimetric changes.

However, protonation of the nitrogen atom adjacent to the ring containing the  $-\text{SO}_3\text{H}$  group preferentially occurs because of the resonance stability of the protonated species (azonium ion) as shown in Scheme 2. This behaviour has been successfully used in the development of epoxy-based azopolymeric sensor bearing methyl orange moieties. Using UV–vis spectroscopy, we monitored the protonation process of activated azo group and hence the colorimetric indicating property towards amines. The UV–vis spectrum of **2** in DMSO/water (8:2, v/v) solution ( $1.25 \times 10^{-2}$  mg/ml, pH 6.85) displayed intense absorption band around  $\lambda_{\text{max}} = 439$  nm typical of  $\pi-\pi^*$  absorption band of azobenzene moiety. A clear indication that protonation of azobenzene nitrogen occurs as depicted in Scheme 3 comes from the UV–vis titration of the

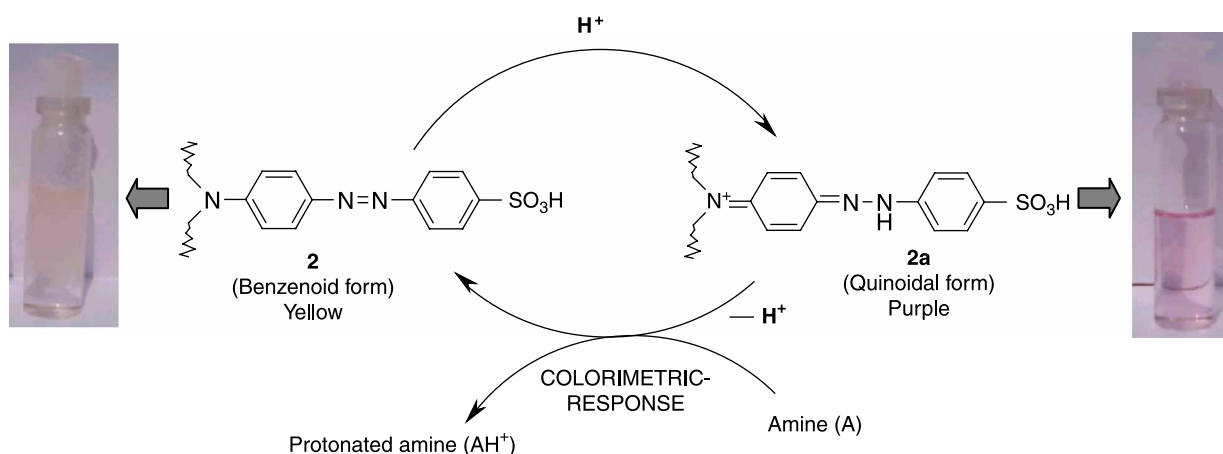
solution of **2** (pH 6.85) with HCl (Figure 1). Upon adding HCl, the intensity of absorption maximum of **2** at 439 nm associated with benzenoid form of azo unit gradually decreased following the appearance of a new band centred at 537 nm associated with the formation of quinoidal form via azonium ion on protonation was observed. The plot of absorbance at 439 nm vs. varied concentration of HCl shows the linear decrease in absorption intensity with HCl concentration of up to 2.0 M and then levels off (Figure 2) with a steep decrease in pH from 6.85 to final pH of 0.95.

A further observation is the presence of an isosbestic point at 500 nm demonstrating the relative presence of benzenoid and quinoidal forms in solution. This change resulted in colour change from light yellow to purple (Scheme 2).

Once protonation has occurred, the colorimetric property of the protonated polymer **2a** towards amines



Scheme 2. Feasible mode of protonation of methyl orange.

Scheme 3. Mode of protonation–deprotonation of **2** and mode of colorimetric indication for amines.

was surveyed with representative amines (*n*-propylamine, dimethylamine, triethylamine, aniline; Figures 3–5). Upon successive addition of amines, the protonated polymer sensor solution showed gradual recovery of absorption band of azobenzene moieties.

This change resulted in the recovery of original colour from purple colour as evidenced from the photograph (Scheme 2). Such an effect on the absorption bands associated with visual colour change could be attributed to the interaction involving proton transfer from polymer bearing azonium ion sites to the amine sites (Scheme 2). As a result, interestingly, the UV–vis spectral response of protonated polymer **2a** was found to show a significant selectivity for the nature of amines as evidenced from the plot of  $(A_q)_0/A_q$  vs. concentration of amines present. Where  $(A_q)_0$  is the absorbance at 537 nm, when the azobenzene moieties are completely in the quinoidal form.  $A_q$  is the absorbance at 537 nm due to quinoidal form in the presence of amine.

The plot shows the more pronounced change in absorption intensity  $(A_q)_0/A_q$  with concentration of aniline compared with the concentration of *n*-propylamine, triethylamine and dimethylamine demonstrating better chemosensitivity of **2a** for aromatic amine, for instance, aniline. The plot further gives an insight into the better chemosensitivity of **2a** towards *n*-propylamine over other representative aliphatic amines. The stronger sensitivity towards aniline was obviously due to the better transfer of proton from azonium ion/quinoidal form to convert aniline into ammonium ion probably correlating with the solvation stabilities of protonated aniline (ammonium ion) associated with the local hydrophobic/hydrophilic balance. This probably suggests further that activated azo dye (methyl orange) units in their protonated form are mostly exposed in the local environment of macromolecular structure promoting better transfer of proton from azonium ion/quinoidal form to aniline. However, under the same conditions, there was no significant spectral change

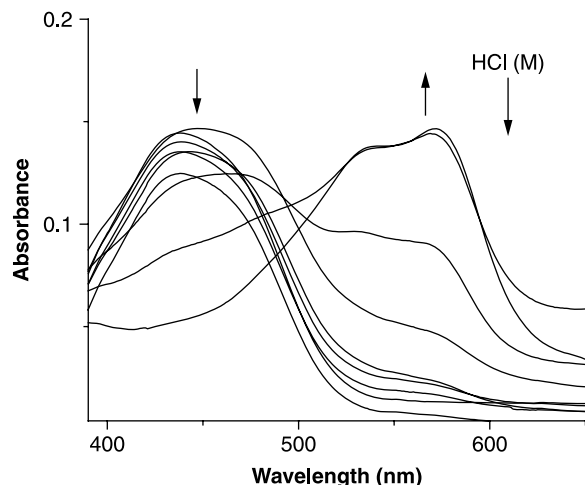


Figure 1. UV-vis spectral change of **2** ( $1.25 \times 10^{-2}$  mg/ml in 8:2 DMSO/H<sub>2</sub>O) in the presence of increasing HCl concentration (M).

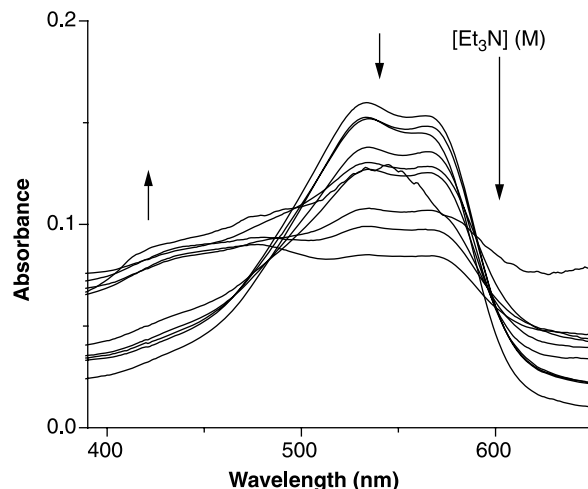


Figure 3. UV-vis spectral change of protonated polymer **2a** (solvent: DMSO/H<sub>2</sub>O (8:2); in the presence of 2.48 M HCl; pH 1.00) upon addition of triethylamine.

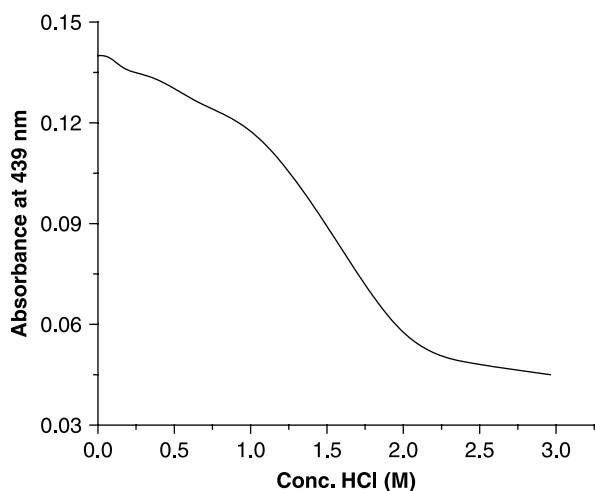


Figure 2. Plot of absorbance at 439 nm vs. varied concentrations of HCl (M).

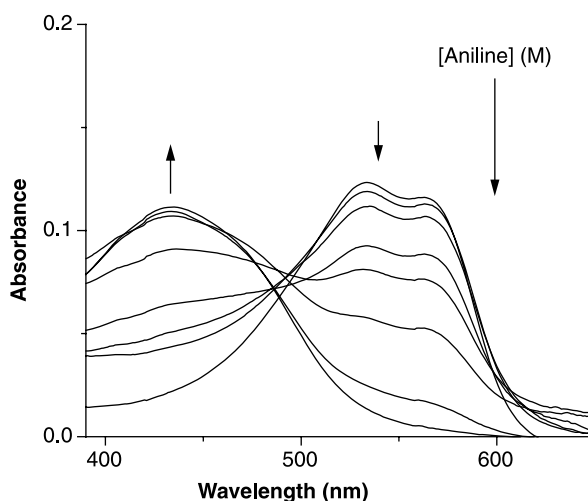


Figure 4. UV-vis spectral change of protonated polymer **2a** (solvent: DMSO/H<sub>2</sub>O (8:2); in the presence of 2.48 M HCl; pH 1.00) upon addition of aniline.

upon the addition of tetrabutylammonium acetate. Even on addition of such acetate salt, protonated polymer **2a** displayed no colorimetric response. We next investigated the changes in pH of the solution of protonated polymer **2a** upon addition of corresponding amines. However, the concept of pH is qualitatively applicable to this situation because the titrations were carried out in DMSO/H<sub>2</sub>O mixture rather than simply water. The pH remained nearly constant spanning a range from 1.00 to 1.60 during the addition of increasing amounts of representative amines (added up to 2.5 M each). Thus, these results suggest that **2a** (protonated form) is a good colorimetric indicator for amines and has a high chemosensitivity among the competing amines.

## Conclusion

In summary, novel epoxy-based azo polymer has been synthesised using post-azo-coupling of poly(hydroxy ether amine) precursor polymer. The amine-sensing behaviour of its stable protonated form has been investigated using representative amines (*n*-propylamine, dimethylamine triethylamine and aniline). More importantly, the amine-sensing and the concomitant absorption changes were clearly visible to the naked eye, as can be seen in the photograph, where the purple solution of protonated polymer **2a** became yellow upon titration with different amines. This finding opens interesting perspectives in the

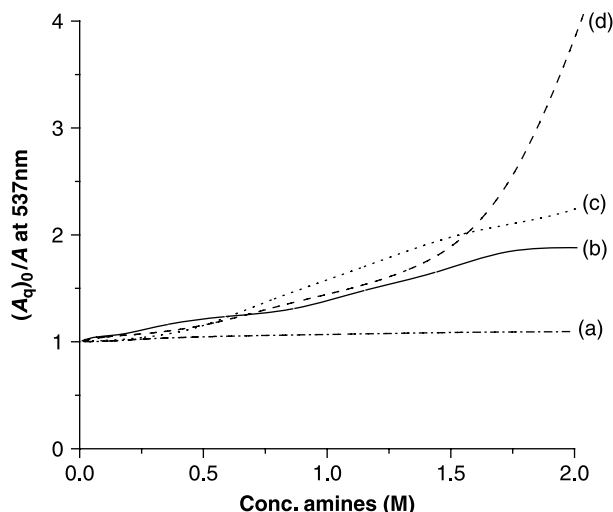


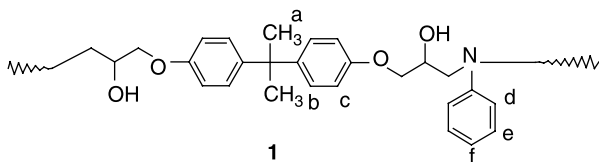
Figure 5. Plot of  $(A_q)_0/A_q$  vs. concentration of amines (M): (a) dimethylamine, (b) triethylamine, (c) *n*-propylamine and (d) aniline.

recognition of amine type of VOCs. Work in this direction is currently under progress.

## Experimental

### Synthesis of 1

Precursor polymer [poly(hydroxy ether amine)] **1** was obtained from the reaction between DGEBA (1.0 g, 2.63 mmol) and aniline (0.25 g, 2.63 mmol) according to the literature (8) at 100°C for 48 h. The product was dissolved in 1,4-dioxan and precipitated with plenty of water. FT-IR (KBr):  $\nu_{\max}$  = 3346 (br, O–H str.), 2965, 2927, 2871 (C–H str. of CH<sub>2</sub> and CH<sub>3</sub> units), 1599, 1505, 1463, 1361 (benzene ring), 1246 (C–O str.), 1107, 1038, 829, 750, 696 cm<sup>-1</sup>.



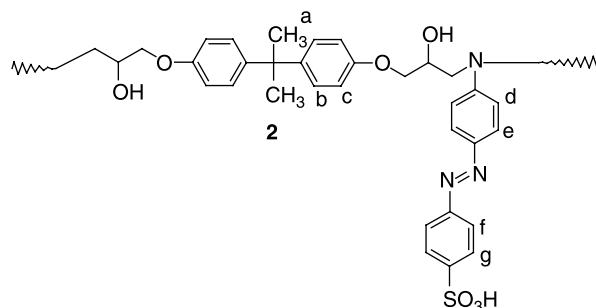
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.19 (m, 3H, H<sub>c</sub>, H<sub>e</sub>), 6.79–6.62 (bs, 3H, H<sub>b</sub>, H<sub>d</sub>, H<sub>f</sub>), 4.29–4.22 (bm, 2H), 3.84–3.70 (bm, 4H), 3.42 (bs, 2H), 3.26–3.31 (bm, 2H), 1.57 (s, 6H) cm<sup>-1</sup>.

### Synthesis of 2

Precursor polymer **1** (1.0 g, 3.32 mmol) was dissolved in DMF (70 ml) at 0°C. A diazonium salt of 4-aminobenzenesulphonic acid was prepared by adding

an aqueous solution of NaNO<sub>2</sub> (0.35 g, 5.05 mmol in 0.25 ml water) into a solution of 4-aminobenzenesulphonic acid (0.5 g, 2.89 mmol in a mixture of 0.25 ml water and 0.42 ml sulphuric acid). The mixture was stirred at 0°C for 2 min and then added dropwise into the solution of **1**. The yellow colour gradually turned into red. The solution was stirred at 0°C for 3 h. Then precipitated with addition of water into the reaction mixture. Precipitate was collected and kept in fresh water for 24 h. The product was then collected, washed with 5% NaOH solution for two times and then washed with water several times, collected and vacuum dried at 50–55°C for 24 h.

FT-IR (KBr).  $\nu_{\max}$  = 3405 (br, O–H str.), 2924 (C–H str. of CH<sub>2</sub> and CH<sub>3</sub> units), 1652 (–N=N– str.), 1600, 1401, 1384 (benzene ring, –SO<sub>2</sub>– str.), 1105, 1093, 1047 (C–O str. –SO<sub>2</sub>– str.), 772 cm<sup>-1</sup>.



<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz).  $\delta$ : 7.95 (s, H<sub>g</sub>), 7.72 (s, H<sub>f</sub>), 7.07 (bs, H<sub>c</sub>, H<sub>e</sub>, proton *meta* to free aniline moiety), 6.81 (d, 8 Hz, H<sub>b</sub>, H<sub>d</sub>), 6.73 (m, proton *ortho* to free aniline moiety), 6.54 (m, proton *para* to free aniline moiety), 4.10–4.04 (bm, 2H), 3.81–3.87 (bm, 4H), 3.73–3.32 (m, 4H), 1.55 (s, 6H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz).  $\delta$ : 162.3, 156.2, 152.0, 151.0, 147.0 (unresolved), 142.7, 129.0, 127.4, 126.6, 124.9, 121.2, 116.2 (unresolved), 113.9, 112.5 (unresolved), 70.0, 69.0, 66.3, 55.5, 54.8, 41.1, 35.8, 30.7.

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