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# Intermolecular charge transfer facilitated synthesis and spectral characterization of Schiff bases of a weak nucleophile 2,3-diamino-1,4-naphthoguinone<sup>†</sup>

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A new synthetic protocol for the formation of novel Schiff bases between a weak nucleophile, 2,3diamino-1,4-naphthoquinone and aldehydes has been developed with addition of hexamethylbenzene (HMB). The driving force for the reaction is the intermolecular CT interaction between HMB and DANQ resulting in enhancement of nucleophilicity as evidenced from spectral and ab initio calculations. The structure of the compounds was confirmed by UV-vis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. The advantages of this procedure are mild reaction conditions, high yield of products, operational simplicity and easy work-up procedures.

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# Introduction

Ever since the discovery of imine formation in 1864 by Hugo Schiff,<sup>1</sup> this classical reaction has been a versatile tool in organic synthesis. Imines have long been the focus of synthetic chemistry due to their dynamic nature and broad spectrum of applications such as build-up of complex molecular architectures,<sup>2</sup> interlocked molecules,<sup>3</sup> in biological chemistry<sup>4</sup> and material areas.<sup>5</sup> They are one of the synthetically important scaffolds for the system of triheteroarylmethanes.<sup>6</sup> The nucleophilic addition of nitro alkanes to the C=N bond of imines known as the aza-Henry reaction is a useful C-C bond forming processes in organic synthesis.<sup>7</sup> Likewise, imines are employed in the synthesis of various compounds such as onestep complex nitrogen heterocycles (poly-cyclic lactam products),<sup>8</sup> piperidines<sup>9,10</sup> and unusual amino acids.<sup>11</sup> The applications of imine compounds in other fields also are well documented viz. metal ions and/or anions sensors,12 organic semiconductors<sup>13</sup> fluorescent and chromogenic probe <sup>14</sup> drug delivery systems<sup>15</sup> and as most celebrated ligands in coordination chemistry.16

Major imine formation procedures involve the condensation of primary amines with carbonyl compounds under conditions which remove water either chemically or physically by using different catalyst and methods such as acetic acid as a catalyst in ethanol,<sup>17</sup> Lewis acid (TiCl<sub>4</sub>),<sup>18</sup> molecular sieves,<sup>19</sup> Dean-Stark apparatus,<sup>20</sup> etc. Most of the reactions proceed in

good yield, while those involving acid-sensitive carbonyl compounds or weak nucleophilic amines can be troublesome, leading to decomposed starting materials or little or no yield.<sup>21</sup> Under such circumstances the purification of the imine is also very difficult. The main objective, therefore, of the present endeavour is to make use of the phenomenon of charge transfer complexation, by a foreign electron donor, in the imine formation between a weak nucleophile, 2,3-diamino-1,4naphthoquinone (1) (DANQ), and aldehydes. Aminonaphthoquinones have a  $\pi$ -conjugated system, a strong intramolecular charge-transfer chromophoric unit and are thus of interest as candidates for non-linear optical materials. Hence, in the present study, it is used as a precursor for the synthesis of Schiff bases.

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## **Result and discussion**

Attempts have been made by us to synthesize imines of the weak nucleophile DANQ with different aldehydes under different conventional conditions and the results obtained are collected in Table 1. The overall reaction is depicted in Scheme 1. The results indicated that all these efforts resulted in either no or very poor yields.

It is presumed that the observed poor/no yields may be due to the very weak nucleophilic nature of the amine. Also it is due to the existence of intramolecular charge transfer transition, from amine to quinone, within the DANQ molecule.<sup>22</sup> The electronic spectrum of DANQ exhibits the characteristic intramolecular CT band at 516 nm (Fig. 1) which is highly solvent dependent<sup>23</sup> (Fig. 2). Both specific and nonspecific solute-solvent interactions were found to influence the absorption maximum. The absorption maximum was

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Synthesis & the UV-vis spectra , Scott plot, Stern–Volmer plot, <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products and molecular orbital structure for HMB and DANO.

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Table 1 Reaction conditions and amounts of imine formed between 1 and representative aldehydes  $(\mbox{2a-2c})^{\rm a}$ 

Reactant	Reagent apparatus	Solvent	Time (h)	Temp. (°C)	Yield (%)
OH O	А	Ethanol	12	78	32
Î Î	В	DCM	12	40	—
	С	DCM	12	40	—
	D	Toluene	12	110	20
	A	Ethanol	12	78	15
	В	DCM	12	40	_
S	C	DCM	12	40	
	D	Toluene	12	110	10
	A	Ethanol	12	78	13
	В	DCM	12	40	_
.O	С	DCM	12	40	_
	D	Toluene	12	110	5

 $^a$  A-Glacial acetic acid; B-TiCl\_4; C-Molecular sieves (4Å); D-Dean–Stark apparatus; DCM-dichloromethane

found to largely depend on the polarity of the medium and observed to increase with an increase in polarity of the medium (see ESI†). Further, from Fig. 1, it is evident that there is no such intramolecular CT transition in the case of 2,3-dichloronaphthaquinone (DCNQ) while it is present in the imine formed with salicylaldehyde, (2E)-2-(2-hydroxybenzylideneamino)-3-aminonaphthalene-1,4-dione (SANQ). Furthermore, on adding increasing amounts of *p*-toluenesulfonic acid to an ethanolic solution of DANQ, the absorbance of the intramolecular CT band decreased indicating a progressive unavailability of the lone pair of electrons on the nitrogen atom of the amino group for the CT transition, as a result of protonation (Fig. 3). It is conceived that if, by some means, one could either remove or relatively decrease the intensity of the



Scheme 1 Condensation of 2,3-diaminonaphthoquinone with aldehydes.



Fig. 1 Electronic absorbance spectra of SANQ, DANQ and DCNQ in ethanol at 298 K.

intramolecular CT transition, the nitrogen atom of the amine moiety would attain sufficient electron density and consequently can form the imine with aldehydes quite easily. To achieve this, a foreign electron donor, hexamethylbenzene (HMB), has been added to the reaction mixture before the addition of the aldehyde.

The selection of HMB is based on the fact that it is inert towards either of the reactants, a relatively good electron donor known to form intermolecular CT complexes with DANQ and it is easily removable from the reaction mixture after completion of the reaction, simply by *n*-hexane washing. In line with our expectations this strategy has been found to work exceedingly well. In order to investigate whether the



**Fig. 2** Electronic spectra of DANQ in various solvents *viz.* a) carbon tetrachloride, b) chloroform, c) ethylacetate, d) THF, e) *tert*-butyl alcohol, f) acetone, g) ethanol, h) methanol, i) dimethylformamide, j) dimethylsulphoxide at 298 K.



Fig. 3 Electronic spectra of DANQ with the addition of pTSA of various concentrations in acetonitrile at 298 K.

added donor HMB has completely overcome or decreased the intensity of the intramolecular CT phenomenon, the interaction between the HMB and DANQ has spectroscopically and theoretically been studied. Incremental addition of HMB to DANQ, decreased the intensity of the intramolecular CT band (Fig. S1<sup>†</sup>) indicating the interaction of HMB with DANQ. To investigate whether the medium or the aldehyde can act as a donor in the formation of intermolecular CT complex with DANQ, representative reactions were also carried out in toluene (Table 1) and in benzene (Table 2). The results indicated that toluene or benzene behaves simply as a medium rather than as an electron donor to the extent to overcome the intramolecular CT interaction. Likewise, an additional equivalent of salicylaldehyde (as a representative case) added to the reaction mixture doesn't alter the percentage yield confirming the non-participation of the aldehyde in the intermolecular CT interaction.

After optimizing the reaction conditions, a variety of aldehydes were also been employed under similar conditions to evaluate the utility of this reaction. The results are shown in Table 2. The aromatic aldehydes carrying both electron withdrawing and electron releasing substituents were also converted to their corresponding imines in good yields. It is noteworthy that the reactions of substituted aldehydes proceeded with the expected good yield and also no undesirable side reactions were observed.

#### UV-Vis absorption spectroscopic study

The interaction between DANQ and HMB was studied using UV-vis spectral technique. The formation constant (K) and molar extinction coefficient ( $\varepsilon$ ) of the 1 : 1 CT complex formed between HMB and DANQ in ethanol, were determined spectrophotometrically using the Scott equation as reported earlier.<sup>24</sup> The values of K and  $\varepsilon$  determined (K = 2180 mol L<sup>-1</sup>; log  $\varepsilon$  = 3.32) from the linear Scott plot (Fig. S2†) suggested that

Table 2 Reaction conditions and amount of imine formed between 1 and (2a-2j) aldehydes in ethanol

Nucleophile	Aldehyde	Temp. (°C)	Yield (%)
	он о	RT RT <sup>a</sup>	94 7
		80"	23
	, 2a	50	92
	, 2b	50	91
	, 2c, 0	50	89
	НОООН		
	, 2d Cl	50	90
0			
NH <sub>2</sub> NH <sub>2</sub>	, 2e CN	50	93
	`O , 2f NO <sub>2</sub>	$50_{70^a}$	90 12
	$\bigcirc$	70	12
	, 2g	DT	06
		$\mathrm{RT}^{a}$ $\mathrm{80}^{a}$	12 16
	, 2h	RT	91
	N		
	, <sup>2i</sup> 0	50	83
	Ĺ		
<sup><i>a</i></sup> In benzene;	, 2j		

the formed CT complex is of strong type.<sup>25,28</sup> Fluorescence spectral technique has also been employed to investigate the interaction between HMB and DANQ (Fig. 4).



**Fig. 4** Fluorescence spectra for the HMB–DANQ system in chloroform at fixed concentration of  $[D] = \{2.375 \times 10^{-3} \text{ M} \text{ (curve D)}\}$  and variable concentrations of  $[A] \times 10^{-5} = \{3.125 \text{ (curve a)}, 6.25 \text{ (curve b)}, 9.375 \text{ (curve c)}, 12.5 \text{ (curve d)}, 15.625 \text{ (curve e)}, 18.75 \text{ (curve f)}\}$  M at 298 K.

The association constant,  $K_f$ , for the HMB–DANQ interaction has been computed using emission data method described by Ward (Fig. S4†). $^{26,28}$  The value of  $K_f$  obtained for the HMB–DANQ system is found to be  $3.09 \times 10^5$  mol  $L^{-1}$  indicating a strong interaction between the constituent partners. The standard Gibbs energy change  $\Delta Go$  was calculated from  $K_f$  using the relation  $\Delta Go = -2.303$  RT  $log_{10}$   $K_f$ . The  $\Delta Go$  value for the system was found to be -31 kJ mol $^{-1}$ , indicating spontaneous interaction between the reaction partners.

Further, the positive deviation observed in the Stern–Volmer plot (Fig. S3<sup>†</sup>) at higher concentrations of DANQ may be due to the simultaneous presence of dynamic and static quenching mechanisms in the interaction between HMB and DANQ.<sup>27,28</sup>

Furthermore, the interaction between HMB and representative imines (**3g** and **3i**) has also been studied by fluorescence methods and the formation constant K<sub>f</sub> calculated are 3.61  $\times$  10<sup>2</sup> and 14.11 mol L<sup>-1</sup> for **3g** and **3i**, respectively. This indicated that the intermolecular charge transfer transition between HMB and imines are relatively weaker than that of HMB-DANQ and which may not be strong enough to derive the formation of imine dimer.

#### Theoretical calculation

*Ab initio* computations were performed (method: RHF/6-311G), without considering the solvent effects for HMB and DANQ molecules. The molecular orbitals (MOs) thus computed are shown in Fig. 5. In the case of DANQ molecule, the energy corresponding to the HOMO and LUMO are -8.8653 and 0.4446 eV, respectively. The energy gap between these two  $MOs^{29}$  is 9.3099 eV which corresponds to the energy needed for the intramolecular CT transition to occur within the molecule. While the energy gap between the HOMO of HMB



Fig. 5 Molecular orbitals of hexamethylbenzene (HMB) and 2,3-diaminonaphthoquinone (DANQ).

(-8.0870 eV) and the LUMO of DANQ (0.4446 eV) is 8.5316 eV which corresponds to the energy required for the formation of  $\pi$ - $\pi^*$  intermolecular CT complex which is relatively less when compared to that required for the intramolecular CT transition. Thus, the intermolecular CT transition  $\pi^*(\text{eg}) \leftarrow \pi(\text{eg})$ , between HMB and DANQ, can occur more easily. Also as these two MOs which are involved in intermolecular CT complex formation possess identical symmetries their overlap is favored to a larger extent. However, this CT transition could not completely overcome the intramolecular CT transition between the amine moiety and quinone, as the energy differences between them are narrow. Thus the intermolecular CT transition is the driving force which makes the amine moiety relatively electron rich and consequently allows formation of the imines with aldehydes.

The energies of the HOMO and the LUMO MOs of the imines (**3a–j**) were also computed by the same method and are collected in Table S1<sup>†</sup>. It is evident from the results that the energy required for intramolecular CT transition to occur in the imines is relatively lower than that required in DANQ. As a result of this, the intramolecular CT transition in **3a–j** can occur easily when compared to that in DANQ. Though the energy required to form intermolecular CT complex between the imines and HMB is comparable with that for DANQ–HMB CT complex, it could not overcome the easy intramolecular CT transition prevailing in the imines. Consequently it prevents the formation of dimeric imines by reacting with another aldehyde molecule. This observation is well supported by the magnitude of the formation constants for these two CT complexes determined by using fluorescence data.

#### Mechanism of the reaction

The plausible mechanism of the imine formation by the weak nucleophile, DANQ, is depicted in Scheme 2. The added foreign donor HMB initially forms an intermolecular CT complex with DANQ. Such a complexation relatively reduced the intensity of intramolecular CT transition between the amine moiety and quinone in the DANQ molecule. This intermolecular CT complexation made the N-atom of the quinone relatively electron rich and consequently assisted the imine formation of the weak nucleophile DANQ with different aldehydes. The reaction conditions and observed yield of the imine formed between DANQ and different aldehydes are



**Scheme 2** Mechanism of intermolecular CT assisted condensation reaction between DANQ and aldehydes.

given in Table 2. Further, when the reaction was carried out in the presence of HMB in ethanol at 40  $^{\circ}$ C it was considerably reduced to less than an hour for all the chosen aldehydes. Also, as expected, after completion of the reaction, HMB can be completely and easily removed from the reaction mixture simply by washing with *n*-hexane in which the imines are insoluble.

### Conclusion

To conclude, the intermolecular CT complex formed between HMB and the weak nucleophile DANQ, assisted the imine formation of the later with different aldehydes. The proposed intermolecular charge transfer assisted synthetic protocol works well for the synthesis of Schiff bases of a weak nucleophile DANQ with variety of aldehydes and is suitable for scale up purposes.

#### **Experimental Section**

General. Commercially available high purity solvents and reagents were used as received. Thin layer chromatography was performed with fluorescent silica coated aluminum sheets. The electronic absorption spectra of the products were recorded on a double beam spectrophotometer (Jasco, Japan V-630) using 1 cm matched quartz cells. The fluorescence spectra were obtained on a spectrofluorimeter (JASCO 6200, Japan). The excitation wavelength was 270 nm and the emission was monitored at 307 nm. The excitation, emission slit width (5 nm) and the scan rate (250 nm) was kept constant for all of the experiments. FT-IR spectra were obtained as KBr pellets (JASCO FT-IR 460 Plus, Japan). Reaction products were characterized by nuclear magnetic resonance spectroscopy (Bruker, <sup>1</sup>H NMR 300 MHz, <sup>13</sup>C NMR 75 MHz). The <sup>1</sup>H NMR spectra data is expressed in the form: Chemical shift in units of ppm (normalized integration, multiplicity, the value of J in Hz).

Synthesis of compounds 3a–j. (2E)-2-(2-Hydroxybenzylideneamino)-3-aminonaphthalene-1,4-dione (3a). To a stirred solution of DANQ (2 g, 0.0106 mol) in 10 mL of ethanol, HMB (1.897 g, 0.0116 mol) was added and the reaction mixture was stirred at RT for 15 min. Afterwards 2-hydroxybenzaldehyde (2a) (2.595 g, 0.0212 mol) was slowly added into the reaction mixture. The reaction mixture was stirred at RT for 1 h and the reaction was monitored by TLC (Thin Layer Chromatography). Once the reaction has been completed 20 mL of *n*-hexane was poured into the crude reaction mixture was filtered through filter paper under vacuum and washed with 20 mL of *n*-hexane to get the pure product as a dark brown solid (1.49 g); Yield = 94%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  12.11 (s, 1H), 9.14 (s, 1H), 7.98 (t, *J* = 9 Hz, 2H), 7.81 (t, *J* = 9 Hz, 1H), 7.73 (m, 2H), 7.39 (t, *J* = 9 Hz, 1H), 7.10 (s, 2H), 6.96 (t, *J* = 6 Hz, 2H).

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  181.3, 176.2, 159.8, 142, 134.7, 132.9, 132.4, 131.6, 130.0, 125.9, 125.3, 122.4, 120.5, 119.1, 116.4.

FT-IR (KBr, cm<sup>-1</sup>) 3430 (OH), 1671, 1604 (C=O), 1577 (HC=N–).

Elemental analysis: Anal. Calcd. for  $C_{17}H_{12}N_2O_3$ : C, 69.86; H, 4.14; N, 9.58. Found: C, 69.31; H, 4.20; N, 10.10.

2-((Thiophene-2-yl)methyleneamino)-3-aminonaphthalene-1,4dione (3b). The procedure followed for the synthesis was the same as that of 3a; (2b) thiophene-2-carbaldehyde (2.383 g, 0.0212 mol) was used instead of 2a and the reaction temperature was changed to 40 °C instead of RT. The final product (3b) was a dark brown solid (1.38 g); Yield = 92%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.44 (s, 1H), 7.96 (t, *J* = 9 Hz, 2H), 7.82 (t, *J* = 6 Hz, 2H), 7.71 (m, 2H), 7.22 (t, *J* = 3 Hz, 6 Hz, 1H), 6.93 (s, 2H).

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  181.2, 177.2, 155.4, 144.1, 143.6, 134.7, 132.6, 132.5, 132.3, 130.9, 130.1, 128.2, 125.9, 125.2, 121.9.

FT-IR (KBr, cm<sup>-1</sup>) 1666, 1603 (C=O), 1573 (HC=N-).

Elemental analysis: Anal. Calcd. for  $C_{15}H_{10}N_2O_2S$ : C, 63.81; H, 3.57; N, 9.92. Found: C, 64.01; H, 3.52; N, 9.90.

2-((Furan-2-yl)methyleneamino)-3-aminonaphthalene-1,4-dione (3c). The procedure followed for the synthesis was the same as that of 3a; (2c) furan-2-carbaldehyde (2.042 g, 0.0212 mol) was used instead of 2b. The final product (3c) was a dark red solid (1.287 g); Yield = 91%

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.25 (s, 1H), 7.99 (m, 3H), 7.82 (t, *J* = 9 Hz, 1H), 7.71 (t, *J* = 9 Hz, 1H), 7.31 (d, *J* = 6 Hz, 1H), 7.09 (s, 2H), 6.72 (m, 1H).

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  181.3, 177.3, 153.3, 149.4, 146.0, 144.3, 134.7, 132.6, 132.3, 130.1, 125.8, 125.2, 121.7, 115.2, 112.6.

FT-IR (KBr, cm<sup>-1</sup>) 1668, 1600 (C=O), 1573 (HC=N-).

Elemental analysis: Anal. Calcd. for C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>: C, 67.67; H, 3.79; N, 10.52. Found: C, 67.39; H, 3.55; N, 10.44.

2-(4-Hydroxy-3-methoxybenzylideneamino)-3-aminonaphthalene-1,4-dione (3d). The procedure followed for the synthesis was the same as that of 3a; (2d) 4-hydroxy-3-methoxybenzaldehyde (3.235 g, 0.0212 mol) was used instead of 2b. The final product (3d) was a brown solid (1.5243 g); Yield = 89%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.80 (s, 1H), 9.15 (s, 1H), 8.08 (d, *J* = 6 Hz, 1H), 7.95 (m, 2H), 7.82 (m, 2H), 7.69 (s, 1H), 7.43 (d, *J* = 6 Hz, 1H), 6.99 (s, 2H), 3.88 (s, 3H).

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  181.4, 176.9, 164.5, 158.5, 155.2, 133.4, 132.9, 132.4, 132.3, 131.5, 129.0, 125.9, 125.3, 120.4, 119.1, 58.6

FT-IR (KBr,  $\rm cm^{-1})$  3320 (OH), 1661, 1603 (C=O), 1566 (HC=N–).

Elemental analysis: Anal. Calcd. for  $\rm C_{18}H_{14}N_2O_4:$  C, 67.07; H, 4.38; N, 8.69. Found: C, 67.21; H, 4.29; N, 8.56.

2-(4-Chlorobenzylideneamino)-3-aminonaphthalene-1,4-dione (3e). The procedure followed for the synthesis was the same as that of 3a; (2e) 4-chloro benzaldehyde (2.979 g, 0.0212 mol) was used instead of 2b. The final product (3e) was a dark brown solid (1.48 g); Yield = 90%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.42 (s, 1H), 8.11 (d, *J* = 6 Hz, 2H), 7.98 (m, 2H), 7.83 (t, *J* = 9 Hz, 6 Hz, 2H), 7.75 (s, 2H), 7.56 (d, *J* = 6 Hz, 2H) .

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  181.3, 177.2, 155.3, 145.8, 140.71, 134.6, 133.1, 132.9, 132.5, 132.4, 132.2, 130.4, 128.9, 125.7, 125.3, 124.5, 121.1.

FT-IR (KBr, cm<sup>-1</sup>) 1669, 1610 (C=O), 1570 (HC=N-).

Elemental analysis: Anal. Calcd. for C<sub>17</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>2</sub>: C, 65.71; H, 3.57; N, 9.02. Found: C, 65.41; H, 3.60; N, 9.17.

4-((3-Amino-1,4-dioxo-1,4-dihydronaphthalen-2-ylimino)methyl)benzonitrile (3f). The procedure followed for the synthesis was the same as that of 3a; (2f) 4-formylbenzonitrile (2.805 g, 0.0212 mol) was used instead of 2b. The final product (3f) was a dark brown solid (1.4890 g); Yield = 93%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.61 (s, 1H), 8.27 (d, *J* = 6 Hz, 2 H), 7.99 (m, 4H), 7.66 (d, *J* = 6 Hz, 2H), 7.45 (s, 2H).

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  181.3, 177.0, 158.3, 145.9, 141.5, 134.9, 133.1, 132.8, 132.5, 132.3, 132.2, 130.0, 128.9, 125.9, 125.3, 124.5, 120.4, 118.7, 112.4.

FT-IR (KBr,  $cm^{-1}$ ) 1672, 1600 (C=O), 1573 (HC=N-).

Elemental analysis: Anal. Calcd. for C<sub>18</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>: C, 71.75; H, 3.684; N, 13.95. Found: C, 71.60; H, 3.58; N, 13.89.

2-(4-Nitrobenzylideneamino)-3-aminonaphthalene-1,4-dione (3g). The procedure followed for the synthesis was the same as that of 3a; (2g) 4-nitro benzaldehyde (3.212 g, 0.0212 mol) was used instead of 2b. The final product (3g) was a dark brown solid (1.536 g); Yield = 90%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.69 (s, 1H), 8.33 (m, 4H), 8.00 (m, 2H), 7.85 (t, *J* = 6 Hz, 9 Hz, 2H), 7.73 (m, 3H).

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  186.6, 181.9, 158.8, 156.6, 145.5, 141.2, 134.1, 133.1, 132.9, 132.6, 132.4, 132.2, 130.3, 128.9, 125.6, 124.7, 123.9, 120.9.

FT-IR (KBr, cm<sup>-1</sup>) 1665, 1620 (C=O), 1570 (HC=N-).

Elemental analysis: Anal. Calcd. for  $C_{17}H_{11}N_3O_4$ : C, 63.55; H, 3.45; N, 13.08. Found: C, 63.36; H, 3.32; N, 13.20.

2-Amino-3-(pyridin-4-ylmethyleneamino)naphthalene-1,4-dione (3h). The procedure followed for the synthesis was the same as that of 3a; (2h) isonicotinaldehyde (2.272 g, 0.0212 mol) was used instead of 2b. The final product (3h) was a dark brown solid (1.41 g); Yield = 96%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.57 (s, 1H), 8.70 (d, *J* = 6 Hz, 2H), 8.00 (m, 4H), 7.85 (m, 1H), 7.73 (m, 3H).

 $^{13}\mathrm{C}$  NMR (DMSO-d<sub>6</sub>, 75 MHz)  $\delta$  181.4, 177.1, 158.09, 150.11, 146.1, 144.0, 135.0, 132.8, 132.3, 130.0, 125.9, 125.4, 122.0, 120.1.

FT-IR (KBr, cm<sup>-1</sup>) 1667, 1610 (C=O), 1560 (HC=N-).

Elemental analysis: Anal. Calcd. for  $C_{16}H_{11}N_3O_2$ : C, 69.31; H, 4.00; N, 15.15. Found: C, 69.43; H, 4.20; N, 15.31.

2-Amino-3-(pyridin-2-ylmethyleneamino)naphthalene-1,4-dione  $(3i)^{30}$ . The procedure followed for the synthesis was the same as that of 3a; (2i) picolinaldehyde (2.272 g, 0.0212 mol) was used instead of 2b. The final product (3i) was a dark brown solid (1.34 g); Yield = 91%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.52 (s, 1H), 8.68 (d, *J* = 6 Hz, 1H), 8.56 (d, *J* = 9 Hz, 1H), 7.98 (m, 2H), 7.87 (m, 2H), 7.73 (t, *J* = 6 Hz, 9 Hz, 1H), 7.55 (s, 2H), 7.46 (t, *J* = 6 Hz, 1H).

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  181.4, 177.1, 160.9, 155.7, 149.3, 145.6, 136.4, 134.9, 132.8, 132.2, 130.0, 126.0, 125.3, 124.9, 121.0, 120.4

FT-IR (KBr,  $cm^{-1}$ ) 1669, 1600 (C=O), 1568 (HC=N-).

Elemental analysis: Anal. Calcd. for C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>: C, 69.31; H, 4.00; N, 15.15. Found: C, 69.43; H, 4.17; N, 15.22.

2-(2-Methylpropyllideneamino)-3-aminonaphthalene-1,4-dione (3j). The procedure followed for the synthesis was the same as that of 3a; (2j) isobutyraldehyde (1.532 g, 0.0212 mol) was used instead of 2b. The final product (3j) was a highly viscous liquid (1.06 g); Yield = 83%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  9.06 (s, 1H), 8.10 (m, 2H), 7.88 (m, 2H), 6.90 (s, 1H), 3.77 (s, 1H), 1.38 (d, *J* = 6.9 Hz, 3H), 1.12 (m, 3H).

 $^{13}\mathrm{C}$  NMR (DMSO-d\_6, 75 MHz)  $\delta$  178.3, 176.2, 163.0, 151.8, 135.5, 133.3, 131.0, 130.7, 130.5, 126.8, 126.3, 126.1, 33.2, 25.4, 24.2.

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