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A Facile Microwave Assisted Neat Synthesis of Bis-amides Using Nano Nickel Copper Ferrite as Amicable Catalyst and Study of their Fluorescence Studies

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ABSTRACT

An efficient and solvent-free approach for various substituted Bis-amides is described. The reaction was performed on the silica surface under microwave conditions. This Microwave Irradiation (MWI) reaction under solvent-free conditions resulted in a "green-chemistry" procedures, by which Bis-amides were synthesized. $NiCuFe_2O_4$ nanoparticle, an efficient and reusable catalyst was employed in the reaction between amide and aldehydes in presence of silica medium to achieve Bis-amides. This approach 'synthesis of the titled compounds in the absence of co-catalyst/additives' is first of its kind. The recoverability and reusability of the catalyst used in the present method was studied. Further the synthesized Bis-amides were subjected for fluorescence studies.

Keywords: Solvent-free, Microwave irradiation, Amides, $NiCuFe_2O_4$, Reusability, Fluorescence

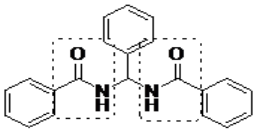
INTRODUCTION

Out of large number of organic dyes hitherto known, there is ongoing effort throughout the world to synthesize new dye laser materials which show improved stability and better efficiency. Apart from their use in basic research in physics and chemistry, they have got wide applications in applied fields, viz., environmental science, medical research and defense etc. Synthesis of new laser dyes is therefore very much required as these may serve as import substitution in view of the potential for their production on industrial scale.

The aim of this paper was to study Bis-amides as push-pull molecules for first-order nonlinear optics and lasing property. Literature survey revealed that bridge-donor-acceptor moiety, were found to be lasing [1-4]. To this purpose, in the present contest three Bis-amide molecules now called as push-pull molecules were synthesized and characterized.

Recently, the synthesis of new dyes with increased cross sections and large unconverted fluorescence has opened up a myriad of various applications viz., push-pull molecules and lasing molecules [5,6]. Two photon optical power limiting, three dimensional optical data storage and photo dynamic therapy, besides three dimensional imaging using two photon laser scanning confocal microscopy. This technique though has high order potential applications had not been examined thoroughly, due to lack of dyes which exhibit high intensity unconverted fluorescence. These investigations will have high utility/applications. When the two photon peak occurs at or near 800 nm, a wave length at which most organic and biological materials have large optical transparency.

Survey literature reveals that Ehrlich et al. had investigated the design of organic two photon materials based on bi-donor containing Stilbene molecule which exhibit the maxima of their two photon absorption at shorter wave length. Reinhart et al., had synthesized a series of numerous molecules with systematically varied structures, which exhibit more effective two photon cross section and characterized in solution using a non-linear transmission technique. The compounds can be categorized into two basic structural families; viz., Donar/bridge/acceptor and Acceptor/donar-donar/Acceptor [7-18].



Donar/bridge/acceptor

In view of this nature of the compounds, Bis-amides were selected for the present investigation; the dyes to be synthesized in this work are first of their kind and have not been studied before for their fluorescence action. These organic compounds having bridge-donor-acceptor moiety are expected to be potential laser dyes and can be prepared in high yields with the possibility of their production on industrial scale.

EXPERIMENTAL

Synthesis and characterization of nano-catalyst

The synthesis and characterization of nano copper ferrite [26] was reported in the literature. In present work nano nickel copper ferrite was synthesized and characterized by X-ray Powder Diffraction (XRD) and Scanning Electron Microscope (SEM) analysis for their structural and morphology studies. The average particle size of nano nickel ferrite was obtained using Scherre's formula was about 13 nm which indicates the synthesized particles were nano crystalline in nature.

General procedure for the synthesis of $NiCuFe_2O_4$

High purity Nickel nitrate, copper nitrate, iron (III) nitrate were employed to synthesize crystalline $NiCuFe_2O_4$ by Co precipitation method. To prepare cationic solutions each starting material was weighed separately and mixed thoroughly. To this cationic solution 0.2 M solution of NaOH was added at 60°C in a thin flow with stirring till the precipitation occurs. The temperature was further increased to 100°C keeping the precipitate in the alkaline condition for 30 min in order to complete the reaction. For the ageing of precipitate the stirring was continued further for 6 h and then the precipitate particles were washed minimum 6 times. The filtered precipitate was dried at 60°C for 48 h. This precipitate was grinded for few minutes using agate mortar pestle to get very fine particles. These particles were heated for 4 h at 1000°C then the nano ferrite particles were formed and they were characterized by XRD and SEM at Andhra University, Visakhapatnam (Figures 1 and 2).

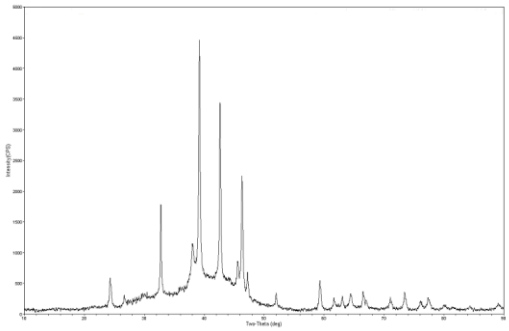


Figure 1: XRD of $NiCuFe_2O_4$

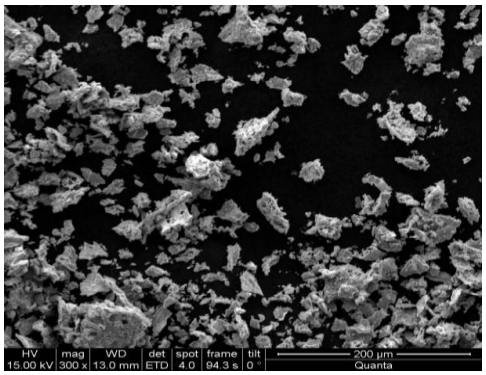


Figure 2: SEM of $NiCuFe_2O_4$

General procedure for the synthesis of Bis-amides (IIIa-IIIc)

A mixture of substituted aromatic aldehydes (1 equation), amide (2 equation), in the medium of silica gel (5 g) and freshly prepared catalyst nano nickel copper ferrite particles (10 mol%) were irradiated under microwave for the time shown in Table 2. The progress of the reaction was continuously monitored by TLC. After the reaction was completed, the mixture was cooled and the solid residue was separated. The solid was dissolved in methanol in order to recover the catalyst by magnetization. After the separation of catalyst the solid was separated and dried in vacuum. The entire synthesized products were characterized by IR, NMR and mass spectroscopic data. The NMR spectra were recorded in Dimethyl Sulfoxide (DMSO-d_6), and the melting points of compounds were compared with authentic samples. The spectral data of these compounds are presented below.

Table 2: Microwave irradiated results

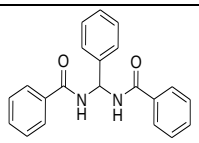
Entry	Product	MWI (medium high)	Time (min)	Yield %	m.p (°C)
1	IIIa	100°C	3	96	235-239
2	IIIb	100°C	4	95	228-232
3	IIIc	100°C	3	95	263-268

Fluorescence measurements

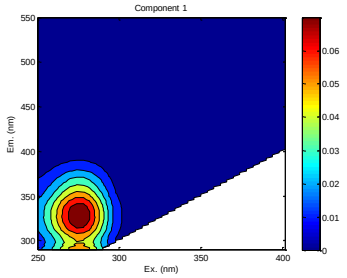
Absorption spectra and excitation spectra of Bis-amides (Compounds IIIa-IIIc) for diluted solutions were measured by a UV-Visible spectrophotometer (Ocean Optics Inc.,) spectrophotometer. The fluorescence experiments were performed at fixed absorbance maxima and fluorescence emission spectra were obtained by using fluoromax. The absorption maxima of IIIa-IIIc were recorded in acetone and presented in Figure 3, the data of emission and the excitation maxima of the molecules were studied and presented in Table 3. The maxima of IIIa-IIIc in acetone showed fluorescence emission at 326 nm, 378 nm and 436 nm respectively, where as they showed fluorescence excitation at 274 nm, 314 nm and 270 nm respectively. From absorption and emission spectra's, the Stokes shifts observed as 52, 64 and 162 nm. The detailed description with Stokes shifts were presented in Table 3. This shows that the functional group of aldehyde enhances and exhibiting high emission values. Hence, it is clearly evident that these molecules are suitable as NLO and biomarkers and further studies are under study regarding the NLO and biomarking.

Table 3: Stokes shifts

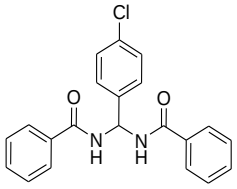
Compound	Solvent	Excitation (nm)	Emission (nm)	Stocks shift (nm)
IIIa	Acetone	274	326	52
IIIb	Acetone	314	378	64
IIIc	Acetone	270	436	162



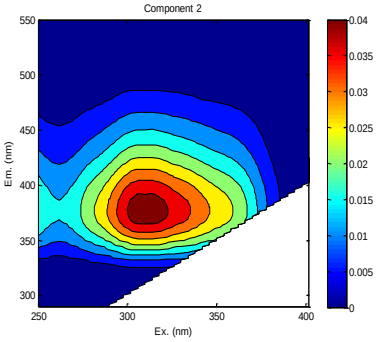
White powder, m.p: 235-239°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm): 7.00-7.03, 7.08-7.89 (15H, m, Ar H), 8.93-9.10 (2H, d, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm): 166.0, 141.3, 133.5, 131.1, 128.0, 126.9, 126.4, 126.0, 58.0.



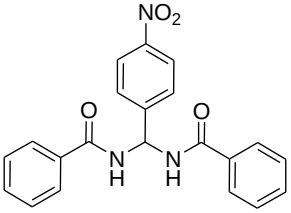
N, N'-(Phenylmethylene) dibenzamide (3a)



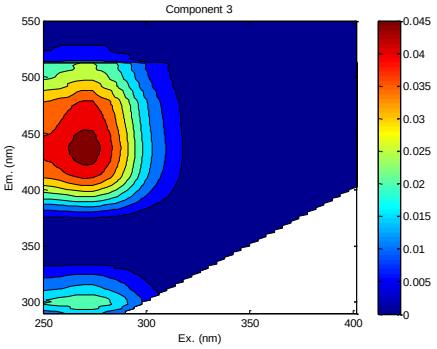
White solid, m.p: 228-232°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm): 7.01-7.04 (1H, m, CH), 7.12-7.13 (1H, m, CH), 7.29 (1H, t, CH), 7.42-7.62 (7H, m, Ar H), 7.88- 7.91 (4H, m, CH), 9.21 (2H, d, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm): 170.6, 149.3, 138.7, 137.2, 133.9, 133.5, 132.6, 132.1, 131.6, 130.5, 130.0, 60.2.



N, N'-(4-Chlorophenylmethylene)dibenzamide (3b)



White solid, m.p: 263-268°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ=7.07 (^{1}H, t, CH), 7.48-7.62 (6H, m, Ar H), 7.76 (2H, CH), 7.95 (4H, d, *J*=7.2 Hz, CH), 8.26 (2H, d, CH), 9.25 (2H, d, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm): 165.5, 147.4, 147.2, 133.4, 131.5, 128.2, 127.9, 127.3, 123.4, 58.3.

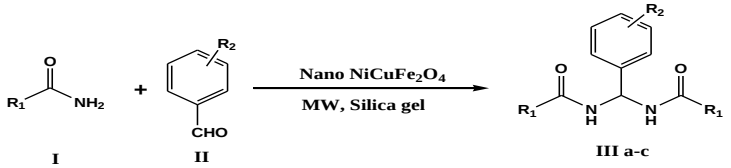


N, N'-(4-Nitrophenylmethylene) dibenzamide (3c)

Figure 3: Spectroscopic data of synthesized Bis-amides

RESULTS AND DISCUSSION

The earlier literature for the synthesis of Bis-amides [19-25] shows some drawbacks hence it is proposed to develop new methodology for the one pot synthesis of bis-amides taking into consideration avoiding toxic chemicals, solvents, reaction time. The usage of a new and efficient catalyst with high catalytic activity, less reaction time, recyclable and with simple work-up procedure for the synthesis of bis-amide and their derivatives would be highly desirable. Considering the above green approaches in this present work, here in it is reported for first time the use of nano $NiCuFe_2O_4$ as heterogeneous support under MWI for the synthesis of Bis-amide and the synthetic scheme is presented in Scheme 1.



R_1: Ar; R_2: a=H; b=*p*-Cl; c=*p*-NO_2

Scheme 1: Synthesis of Bis-amide

All the process of synthesis were obtained by treating Compound I (2 mmol), Compound II (1 mmol), using nano-catalyst $NiCuFe_2O_4$ in silica gel medium (5 g). The conditions of temperature and amount of nano-catalyst required for this synthetic approach was investigated and it was found that the catalyst worked more efficiently at optimized quantity of 10 mmol and producing product yields up to 93%.

In all the reactions, the reaction between substituted aromatic aldehyde's with either electron-donating or electron-withdrawing groups and substituted amides processed smoothly and produced products in excellent yield. For the above reactions the reaction times, yields of products and their melting points.

The structural characterization of synthesized compounds was done by IR, ^{1}H-NMR, ^{13}C-NMR spectra and the synthesized compounds were also confirmed by their melting points and spectral data of authentic samples. Further the reusability of the $NiCuFe_2O_4$ was studied. For this purpose after completion of the each reaction, the reaction mixture was cooled and filtered. The catalyst was separated by magnetization process and used for five subsequent runs. The yields of products were recorded in each run and observed that the yields were slightly decreased after four runs. The results are shown in the Table 1.

Table 1: Study on reusability of nano-catalyst

Entry	Catalyst recovery (%)[a]	Yield (%)[b]
1	-	98
2	90	95
3	87	89
4	84	85

[a]Catalyst recovered by membrane filtration and washed with acetone and then by distilled water; [b]Yields compared to isolated products

CONCLUSION

Finally, heterogeneous nano nickel copper ferrite catalyst was prepared for the synthesis of Bis-amides and their derivatives with short reaction time without using any acidic catalyst, toxic materials or solvents. In addition, the process offers an advantage of easy separation of the nano $NiCuFe_2O_4$ from the reaction mixture, which can be reused and recyclable without any significant degradation of catalytic activity.

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