

APPLICATION of SBA-Pr-SO₃H IN THE GREEN SYNTHESIS OF ISATINHYDRAZONE DERIVATIVES: CHARACTERIZATION, UV-Vis INVESTIGATION AND COMPUTATIONAL STUDIES

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ABSTRACT

An efficient and green synthesis is developed for the preparation of the arylidene isatinhydrazone derivatives **4a-m** using a heterogeneous mesoporous acid catalyst of SBA-Pr-SO₃H with a pore size of 6 nm under solvent free conditions. The hydrazones **4a-m** were then analyzed by UV-Vis spectroscopy and the results were used for the calculation of the HOMO-LUMO band gap. In addition, the quantum chemical calculations were performed to provide an illustrative explanation for the obtained band gap; it is found that probably these molecules have a high tendency to donate electrons to the appropriate small-molecule acceptors with low energy and empty molecular orbital.

Keywords: Arylidene isatinhydrazone, SBA-Pr-SO₃H, Green synthesis, HOMO-LUMO band gap, Small-molecule acceptors.

INTRODUCTION

Hydrazone compounds are usually named after aldehydes and ketones from which they are obtained. Hydrazones are one of the most important and widespread classes of analytical reagents for the determination of different metal ions using various analytical techniques.¹ In addition, they have vast biological properties for the treatment of tuberculosis, leprosy and mental disorders.² For example, isonicotinoyl hydrazones are significant antitubercular agents.³ Some of hydrazones are also good insecticides, rodenticides, nematocides and plant growth regulators.⁴ Isatinhydrazones as versatile Schiff bases can form a variety of complexes^{5,6} and have different biological activities for instance antimicrobial,⁷ antiglycation⁸ and antiproliferative⁹ activities.

Santa Barbara Amorphous (SBA-15) mesoporous silica was synthesized for the first time in 1998 by Zhao and coworkers.^{10,11} SBA-15 is a hexagonal mesoporous silica with good accessibility due to its high surface area, large pore size, excellent stability (chemical and thermal), and easy isolation from the products.^{12,13} The surface of SBA-15 can be modified with various functional groups.¹⁴⁻¹⁸ In continuation of our previous studies,¹⁹⁻²⁵ herein, we used the propyl sulfonic acid functionalized SBA-15 (SBA-Pr-SO₃H) as a heterogeneous solid acid catalyst in the synthesis of isatinhydrazone derivatives. Additionally, at the present work, the relation between the structure and spectral properties are determined through UV-Vis spectroscopy as well as quantum chemical calculations. Then, the HOMO-LUMO analysis of isatinhydrazone compounds are investigated. Moreover, the calculated results are compared with the experimental results.

EXPERIMENTAL

The chemical compounds which were employed in this work, obtained from Merck Company and used with no purification. Melting points were measured by capillary tube method with an Electrothermal 9200 apparatus. Infrared (IR) spectra were recorded from KBr disks using a Fourier-transform (FT)-IR Bruker Tensor 27 instrument. ¹H NMR (250 MHz) and ¹³C NMR (62.5 MHz) spectra were run on a Bruker DPX using tetramethylsilane (TMS) as internal standard in CDCl₃ and/or DMSO-d₆ solution. Mass spectrometry (MS) analysis was performed on a model 5973 mass-selective detector (Agilent). UV-Vis spectrum was run on Analytik Jena Specord® S600 spectrophotometer. Scanning electron microscopy (SEM) analysis was performed on a Philips XL-30 field-emission scanning electron microscope operated at 16 kV, while transmission electron microscopy (TEM) was carried out on a Tecnai G2 F30 at 300 kV.

Quantum chemical calculations

All of the quantum chemical calculations were accomplished using Molecular Orbitals theory (Hückel calculation) via the ChemBioOffice 2008 (Ultra 11.0).

Synthesis and functionalization of SBA-15

The mesoporous SBA-15 was synthesized and functionalized according to our previous publication¹⁹ and then, the obtained SBA-Pr-SO₃H was used as a mesoporous solid acid catalyst in the following reaction.

Synthesis of 3-Hydrazoneindolin-2-one (2)

A mixture of isatin **1** (10 mmol, 1.47 g) and hydrazine monohydrate (80%, 5 ml) were heated under reflux condition. When the yellowish product was observed and the reaction completed (monitored by TLC, 30 min), the mixture was diluted with water and then, the product was dissolved in ethyl acetate (3×20 ml). The organic phases were dried over MgSO₄, filtered and the solvent was evaporated in *vacuo* to obtain the pure product.

3-Hydrazoneindolin-2-one (2)

Yellow powder, FT-IR (KBr): ν = 3356, 3153 (NH₂), 1686 (C=O), 1655 (NH), 1587, 1550 and 1465 (aromatic C-C). ¹H NMR (250 MHz, DMSO-D₆): δ_{H} = 6.8 (d, *J*=7.5, 1H, Ar-H), 6.9 (t, *J*=7.5, 1H, Ar-H), 7.1 (t, *J*=7.5, 1H, Ar-H), 9.5 (s, 1H, NH), 10.5 (s, 2H, NH₂) ppm.

General procedure for the synthesis of arylidene isatinhydrazones (4a-m)

The SBA-Pr-SO₃H (0.02 g which contains 0.024 mmol of loaded -SO₃H) was activated in vacuum at 100 °C and then, after cooling to room temperature, isatinhydrazone **2** (0.161 g, 1 mmol) and aldehyde derivatives (1 mmol) were added to it. The mixture was heated in an oil bath (120 °C) in appropriate time as shown in Table 2. After completion of the reaction which was monitored by TLC, the crude product was dissolved in hot EtOH and then filtered to remove the solid catalyst. The filtrate was cooled to give the pure product. The solid acid catalyst subsequently was washed with hot EtOH, diluted acid solution, distilled water and acetone, and dried under vacuum. It can be used for several times without loss of significant activity.

3-(Benzylidenehydrazone)indolin-2-one (4a)

Red powder, 3161 (NH), 3088 (aromatic C-H), 1728 (C=O), 1613 (NH), 1585, 1553 and 1458 (aromatic C-C). ¹H NMR (250 MHz, CDCl₃): δ_{H} = 6.9 (d, *J*=8, 1H, Ar-H), 7.1 (t, *J*=7.75, 1H, Ar-H), 7.38 (t, *J*=7.75, 1H, Ar-H), 7.5 (d, *J*=4, 3H), 7.9 (m, 2H), 8.1 (d, *J*=7.75, 1H, Ar-H), 8.5 (s, 1H, -N=CH-Ar), 8.6 (s, 1H, NH) ppm.

3-((3-Methoxybenzylidene)hydrazone)indolin-2-one (4g)

Brownish red crystal, 3171 (NH), 3090 (aromatic C-H), 2967 and 2857 (CH₃), 1738 (C=O), 1616 (NH), 1593, 1544 and 1489 (aromatic C-C). ¹H NMR (250 MHz, CDCl₃): δ_{H} = 3.9 (s, 3H, OCH₃), 6.9-7.1 (m, 3H, Ar-H), 7.3-7.4 (m, 4H, Ar-H), 8.1 (d, *J*=7.5, 1H, Ar-H), 8.5 (s, 1H, -N=CH-Ar), 9.65 (s, 1H, NH) ppm. ¹³C NMR (62.5 MHz, CDCl₃): δ_{C} = 55.4 (OCH₃), 111.1, 113.2, 117.1, 118.2, 122.2, 123.2, 129.6, 130.0, 133.5, 134.9, 143.8, 151.2, 160.0, 161.9, 166.8 ppm. MS (m/e): 280 (M⁺+1, 4%), 279 (M⁺, 8%), 251 (100%), 236 (45%), 208 (15%), 118 (30%), 92 (30%), 77 (35%).

3-((3-Nitrobenzylidene)hydrazone)indolin-2-one (4i)

Orange powder, 3159 (NH), 3085 (aromatic C-H), 1743 (C=O), 1617 (NH), 1594, 1531 and 1460 (aromatic C-C). ¹H NMR (250 MHz, DMSO-D₆): δ_{H} = 6.9 (d, *J*=22, 2H, Ar-H), 7.4 (s, 1H, Ar-H), 7.7 (m, 2H, Ar-H), 8.4 (s, 2H, -N=CH-Ar), 8.6 (s, 2H, Ar-H), 10.9 (s, 1H, NH) ppm. ¹³C NMR (62.5 MHz, DMSO-D₆): δ_{C} = 111.4, 116.5, 122.9, 123.9, 126.5, 129.1, 131.2, 134.4, 134.5, 135.4, 145.6, 148.7, 150.4, 157.3, 164.7 ppm. MS (m/e): 294 (M⁺, 10%), 266 (100%), 220 (50%), 145 (15%), 118 (85%), 103 (45%), 91 (40%), 76 (55%).

3-((3-Phenylallylidene)hydrazone)indolin-2-one (4l)

Yellow powder, 3148 (NH), 3094 (aromatic C-H), 3043 (=C-H), 1724 (C=O), 1623 (NH), 1603, 1543 and 1473 (conjugated and aromatic C-C). ¹H

NMR (250 MHz, CDCl_3): δ_{H} = 5.9 (s, 1H, *trans* -CH=CH-Ph), 6.4 (d, $J=1.75$, 1H, =CH-CH=CH-Ph), 6.8 (d, $J=7.75$, 1H, -N=CH-), 7.0 (m, 2H, Ar-H), 7.2 (m, 1H, Ar-H), 7.45 (m, 3H, Ar-H), 7.6 (m, 3H, Ar-H), Ar-H, 8.7 (s, 1H, NH). ^{13}C NMR (62.5 MHz, $\text{DMSO}-d_6$): δ_{C} = 77.2, 106.4, 110.8, 122.9, 124.4, 125.9, 128.9, 129.1, 129.4, 129.9, 130.0, 140.7, 141.3, 145.8, 174.1 ppm. MS (m/e): 276 ($M^+ + 1$, 25%), 275 (M^+ , 100%), 247 (90%), 157 (40%), 144 (85%), 132 (60%), 77 (50%).

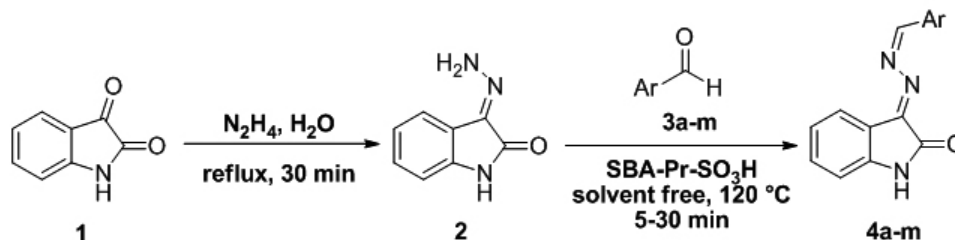
RESULTS AND DISCUSSION

Functionalization of SBA-15 and its analysis

Mesoporous SBA-15 was prepared by using commercially available triblock copolymer Pluronic P126 as a structure-directing agent.^{10,11} Then, the surface of SBA-15 was firstly functionalized with (3-mercaptopropyl) trimethoxysilane (MPTS) and followed by the oxidation of thiol groups to sulfonic acid using hydrogen peroxide.²⁶ As shown in Fig. 1, The SEM image shows uniform particles about 1 μm as same morphology as SBA-15. It illustrates that no changes occurred during the surface modifications and morphology of the solid was remained. In addition, the TEM image exhibits parallel channels that resemble the pore configurations of SBA-15. This reveals that the pores of SBA-Pr-SO₃H were not collapsed during the two-step modification reaction.

Synthesis of isatinhydrazones

In this paper, isatinhydrazone **2** was initially synthesized by the reaction of isatin **1** with excess amount of hydrazine monohydrate under reflux condition in 30 minutes (Scheme 1). Then, a simple and highly efficient strategy for the synthesis of arylidene isatinhydrazones was performed by the reaction of obtained isatinhydrazone **2** and aromatic aldehydes **3a-m** in the presence of SBA-Pr-SO₃H (Scheme 1). To optimize the reaction conditions, isatinhydrazone **2** and benzaldehyde **3a** were subjected to the various conditions using a catalytic amount of SBA-Pr-SO₃H. As shown by the results in Table 1, among the tested solvent-free systems, the best result was achieved in the presence of SBA-Pr-SO₃H, with the shortest reaction time (5 min) in high yield of the product. Nevertheless, the effect of solvents was also investigated for this reaction in which the catalyst was not effective as well as a solvent free system. Furthermore, the weak catalytic role of pure SBA-15 (Entry 6, Table 1) in this reaction emphasizes to this fact that the sulfonic acid functional groups onto the surface of SBA-15 accelerate the reaction. Thus, the higher yields of this reaction are attributed to the effect of the nanopore size of about 6 nm of SBA-Pr-SO₃H, which could act as a nanoreactor.



Scheme 1: Synthesis of isatinhydrazone **2** and its derivatives **4a-m**

Table 1: The optimization of reaction condition for the synthesis of benzylidene isatinhydrazone **4a**.

Entry	Solvent	Catalyst	Temperature (°C)	Time	Yield (%)
1	-	-	120	1 h	80
2	-	SBA-Pr-SO ₃ H*	120	5 min	95
3	-	SBA-Pr-SO ₃ H*	rt	5 days	90
4	EtOH	SBA-Pr-SO ₃ H*	reflux	2/5 h	85
5	H ₂ O	SBA-Pr-SO ₃ H*	reflux	4 h	N.R.
6	-	SBA-15*	120	1 h	85

*0.02 g

In order to evaluate the generality and versatility of this methodology, isatinhydrazone **2** and aromatic aldehydes **3a-m** in a molar ratio of 1:1 were used in the optimum quantity of SBA-Pr-SO₃H (0.02 g). Different arylidene isatinhydrazone derivatives **4a-m** were prepared successfully under solvent-free condition. The results were good in terms of the reaction times and yields and were summarized in Table 2. When the reaction was completed, the crude

product was dissolved in hot EtOH, and the catalyst was separated by a simple filtration and reactivated by washing with hot EtOH and subsequently with a dilute acid solution, water, and acetone for reusing without noticeable loss of reactivity. The new products were characterized by Mass, FT-IR and NMR spectroscopy data.

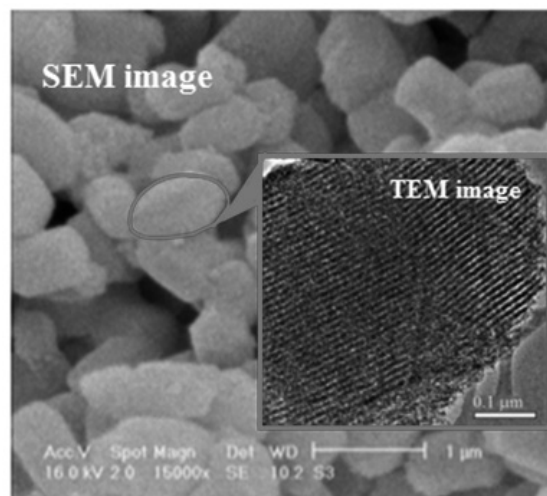



Fig. 1: SEM and TEM images of SBA-Pr-SO₃H

Table 2: Synthesis of arylidene isatinhydrazones **4a-m** in the presence of SBA-Pr-SO₃H as catalyst.

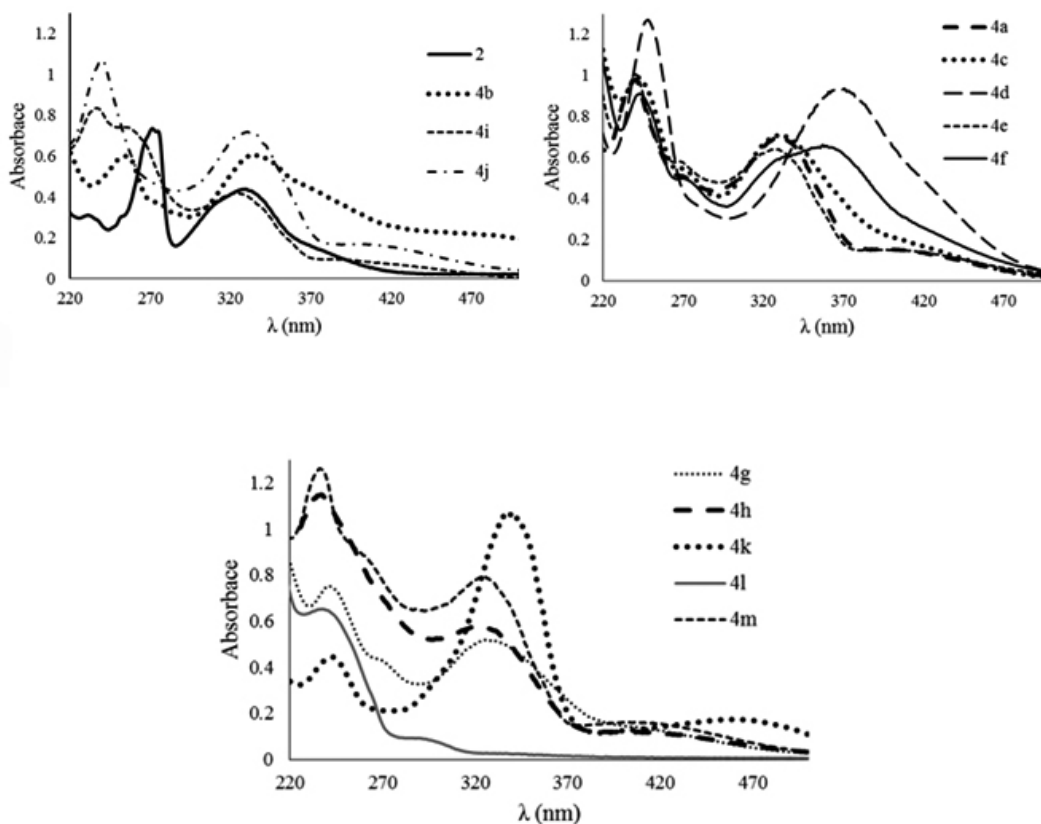
Entry	No.	Ar	Time (min)	Yield (%)	m.p. (°C)
1	4a	Ph	5	98	197-200
2	4b	2-OH-C ₆ H ₄	5	98	208-211
3	4c	3-OH-C ₆ H ₄	10	85	242-245
4	4d	4-OH-C ₆ H ₄	5	90	275-276
5	4e	3-Cl-C ₆ H ₄	15	90	209-210
6	4f	2-OMe-C ₆ H ₄	10	88	168-171
7	4g	3-OMe-C ₆ H ₄	15	85	217-220
8	4h	2-NO ₂ -C ₆ H ₄	25	95	256-257
9	4i	3-NO ₂ -C ₆ H ₄	15	88	260-262
10	4j	4-F-C ₆ H ₄	5	85	257-260
11	4k	4-(NMe ₂)-C ₆ H ₄	10	80	209-212
12	4l	cinnamyl	5	95	200-202
13	4m		30	95	225-227

There are only a few reports for the synthesis of arylidene isatinhydrazone derivatives **4** in which the product was obtained in an acidic condition (HCl and/or H₂SO₄) under refluxing for 3-5 h.⁶⁻⁸ In comparison with the existing methods, the present methodology has several advantages such as greener condition, shorter reaction time, easy work-up, and good yield with high product purity.

UV-Vis spectroscopy and quantum chemical calculations

The experimental maximum absorption wavelengths (λ_{\max}) were found for isatinhydrazone **2** and arylidene isatinhydrazone derivatives **4a-m** in ethanol as

solvent (Chart 1). The two λ_{\max} of isatinhydrazone **2** were observed at 275 and 330 nm (Chart 1-a), which are attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions, respectively. Among the arylidene isatinhydrazone derivatives, compounds **4a-j** and **4l-m** almost showed a similar UV-Vis spectrum, whereas **4k** was completely different. For example, compound **4a** exhibited two absorptions at 241 and 334 nm (see Chart 1b) related to the $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions, respectively; while compound **4k** shows these transitions at 342 and 243, respectively (see Chart 1c).

**Chart 1:** UV-Vis spectrum of isatinhydrazone **2** and arylidene isatinhydrazone derivatives **4a-m** in EtOH.

The quantum chemical calculations of the compounds **2** and **4a-m** were performed using Molecular Orbitals theory (Hückel calculation) *via* the ChemBioOffice 2008 to determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) providing useful additional insights into the possibility of electron transfer between HOMO and LUMO of the molecules. The corresponding HOMO and LUMO density distributions of the compounds **2** and **4a** are presented in Fig. 2. In HOMO structure of **2**, it is evident that the HOMO electron density is more distributed on the nitrogen atoms of hydrazone moiety and some of the carbon

atoms, however, in LUMO structure, the density is diffused on the all atoms. In HOMO structure of **4a**, the density of electrons is distributed on the carbonyl group and the nitrogen atoms of hydrazone moiety, but the LUMO structure shows the electrons are distributed on the phenyl group. Therefore, the carbon atoms in the C=N bond of the hydrazone moiety and the carbonyl group (in the ground state of the molecules) are the active sites for the absorption of the photons from the UV-Vis irradiation to convert the molecule from the HOMO to LUMO form.

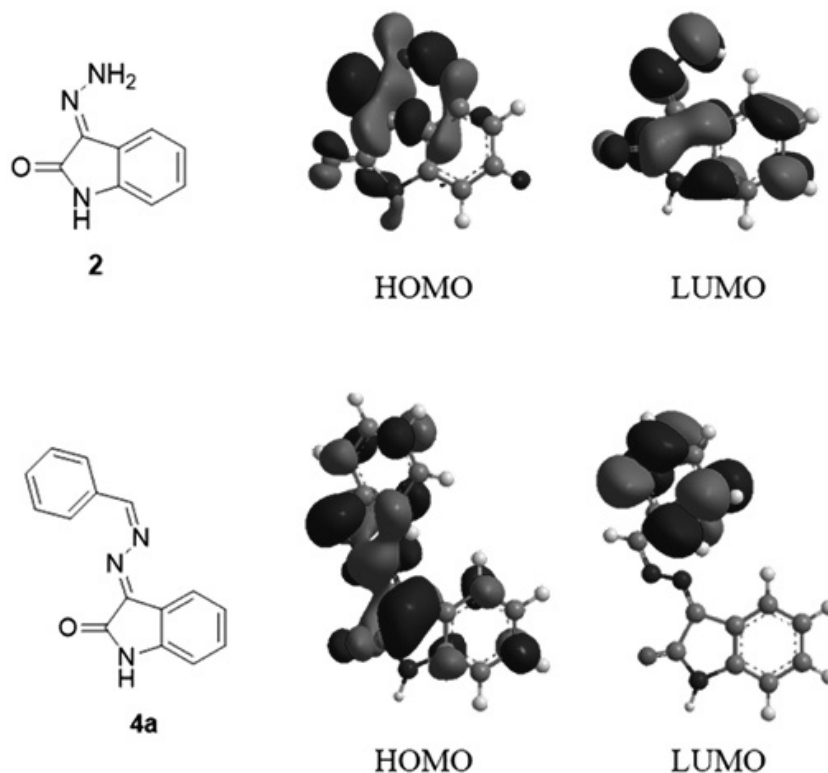


Fig. 2. Frontier molecular orbital density distributions of compounds **2** and **4a**

E_{HOMO} is related to the electron donating ability of the molecule. The high value of E_{HOMO} indicates the molecule tendency to donate electrons. E_{LUMO} shows the ability of the molecule to receive electrons in which lower values of E_{LUMO} are more probable to accept electrons. Herein, the quantum chemical parameters such as the energy of the HOMO and LUMO orbitals and the band gap energy of **2** and **4a-m** were calculated and are comprised with the calculated

band gap energy, ΔE , from the λ_{max} (Table 3). The λ_{max} was obtained from the UV-Vis spectra of each compound in EtOH (Chart 1). According to the prior studies about the electron donating molecules,²⁷⁻³⁰ and based on the results in Table 3, the high values of E_{HOMO} for the molecules probably suggests that these molecules have high tendency to donate electrons to a proper acceptor molecule with low energy and empty molecular orbital.

Table 3: The quantum chemical parameters derived from compounds **2** and **4a-m**.

Entry	Compound No.	λ_{max} *(nm)	HOMO-LUMO gap (ev) from $E=hc/\lambda_{\text{max}}$	HOMO predicted (ev)	LUMO predicted (ev)	HOMO-LUMO gap (ev) Predicted
1	2	275	4.51	-7.86	-1.86	6.00
2	4a	241	5.15	-6.259	-1.12	5.14
3	4b	256	4.84	-5.00	-0.527	4.47
4	4c	241	5.15	-6.21	-0.83	5.38
5	4d	247	5.02	-5.90	-1.07	4.83
6	4e	240	5.17	-6.21	-0.83	5.38
7	4f	242	5.13	-6.08	-0.52	5.6
8	4g	241	5.15	-6.20	-0.83	5.37
9	4h	237	5.24	-7.06	-4.72	2.34
10	4i	233	5.33	-6.54	-5.28	1.26
11	4j	275	4.5	-5.89	-1.07	4.82
12	4k	342	3.63	-5.12	-1.02	4.10
13	4l	237	5.23	-6.91	-2.23	4.68
14	4m	236	5.26	-6.21	-1.05	5.16

*obtained from UV-Vis spectra

CONCLUSIONS

A highly efficient method for the synthesis of arylidene isatinhydrazones **4a-m** has been developed in the solvent free reaction of isatinhydrazones **2** and different aldehydes **3a-m** using recyclable, environmentally benign and green heterogeneous nano catalyst of SBA-Pr-SO₃H. The simplicity of the reaction, recovery of the nano solid acid catalyst without loss of reactivity, and high yield of the products offer improvements over existing methods. Then, the absorption spectra of the hydrazones **4a-m** were obtained by UV-Vis spectroscopy and the results were used for calculation of the HOMO-LUMO band gap. In order to investigate the molecular orbitals of the products, the quantum chemical calculations were performed. The results were compared with the obtained HOMO-LUMO band gap from UV-Vis spectra and it was found that probably these molecules have a high tendency to donate electrons to the appropriate small-molecule acceptors with low energy and empty molecular orbital.

ACKNOWLEDGMENT

We gratefully acknowledge the financial support from the Research Council of Alzahra University and the University of Tehran.

REFERENCES

- 1.- R. B. Singh, P. Jain, R. P. Singh, *Talanta*, **29**, 77, (1982).
- 2.- P. K. Yu, I. B. Boris, T. V. Troepol'skaya, *Russ. Chem. Rev.*, **39**, 441, (1970).
- 3.- D. Sriram, P. Yogeeswari, K. Madhu, *Bioorg. Med. Chem. Lett.*, **15**, 4502, (2005).
- 4.- L.N. Suvarapu, Y.K. Seo, S.-O. Baek, V.R. Ammireddy, *E-J. Chem.*, **9**, 1288, (2012).
- 5.- N. Raman, K. Pothiraj, T. Baskaran, *J. Coord. Chem.*, **64**, 3900, (2011).
- 6.- M. Rabia, A. Mohamad, N. Ismail, A. Mahmoud, *Russ. J. Gen. Chem.*, **83**, 2502, (2013).
- 7.- M. Rabia, A. Mohamad, N. Ismail, A. Mahmoud, *J. Iran. Chem. Soc.*, **11**, 1147, (2014).
- 8.- K. M. Khan, M. Khan, M. Ali, M. Taha, S. Rasheed, S. Perveen, M.I. Choudhary, *Bioorg. Med. Chem.*, **17**, 7795, (2009).
- 9.- T.A.-F.M. Hassan, A.A. Kadi, H.A.-K. Abdel-Aziz, in US 20120252860A1, King Saud, pp. 19, 2013.
- 10.- D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science*, **279**, 548, (1998).
- 11.- D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.*, **120**, 6024, (1998).
- 12.- K. Bahrami, M.M. Khodaei, P. Fattahpour, *Catal. Sci. Technol.*, **1**, 389, (2011).
- 13.- R.V. Grieken, J.A. Melero, G. Morales, *J. Mol. Catal. A: Chem.*, **256**, 29, (2006).
- 14.- B. Karimi, M. Vafaezadeh, *Chem. Commun.*, **48**, 3327, (2012).
- 15.- A.S. Maria Chong, X.S. Zhao, *J. Phys. Chem. B*, **107**, 12650, (2003).
- 16.- S. Fiorilli, B. Onida, B. Bonelli, E. Garrone, *J. Phys. Chem. B*, **109**, 16725, (2005).
- 17.- B. Karimi, E. Badreh, *Org. Biomol. Chem.*, **9**, 4194, (2011).
- 18.- G. Mohammadi Ziarani, A. Badiei, S. Mousavi, N. Lashgari, A. Shahbazi, *Chin. J. Catal.*, **33**, 1832, (2012).
- 19.- P. Gholamzadeh, G. Mohammadi Ziarani, A. Badiei, Z. Bahrami, *Eur. J. Chem.*, **3**, 279, (2012).
- 20.- P. Gholamzadeh, G. Mohammadi Ziarani, A. Badiei, A. Abolhassani Soorki, N. Lashgari, *Res. Chem. Intermed.*, **39**, 3925, (2013).
- 21.- G. Mohammadi Ziarani, R. Moradi, A. Badiei, N. Lashgari, B. Moradi, A.A. Soorki, *J. Taibah Univ. Sci.*, **9**, 555, (2015).
- 22.- G. Mohammadi Ziarani, N. Lashgari, A.R. Badiei, *Scientia Iranica*, **20**, 580, (2013).
- 23.- G. Mohammadi Ziarani, N. Lashgari, A. Badiei, *J. Mol. Catal. A: Chem.*, **397**, 166, (2015).
- 24.- G. Mohammadi Ziarani, N. H. Mohtasham, A. Badiei, N. Lashgari, *J. Chin. Chem. Soc.*, **61**, 990, (2014).
- 25.- N. Lashgari, G. Mohammadi Ziarani, A. Badiei, M. Zarezadeh-Mehrzi, *J. Heterocycl. Chem.*, **51**, 1628, (2014).
- 26.- G. Mohammadi Ziarani, A. Badiei, Y. Khaniania, M. Haddadpour, *Iran. J. Chem. Chem. Eng.*, **29**, 1, (2010).
- 27.- F. N. Ajeel, A. M. Khudhair, A.A. Mohammed, *Int. J. Sci. Res.*, **4**, 2334, (2015).
- 28.- G. Tian, D. Wu, S. Qi, Z. Wu, X. Wang, *Macromol. Rapid Commun.*, **32**, 384, (2011).
- 29.- E. Y. H. Teo, Q.D. Ling, Y. Song, Y.P. Tan, W. Wang, E.T. Kang, D.S.H. Chan, C. Zhu, *Org. Electron.*, **7**, 173, (2006).
- 30.- M. Bozorg, T. Shahrabi Farahani, J. Neshati, G. Mohammadi Ziarani, Z. Chaghazardi, P. Gholamzadeh, F. Ektefa, *Res. Chem. Intermed.*, **41**, 6057, (2015).