PHOTOSWITCHABLE HEXAARYLBIIMIDAZOLES FOR POTENTIAL USE IN SWITCHING TECHNOLOGIES APPLICATIONS

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Abstract— We report the synthesis and optical properties of a novel hexaarylbiimidazoles (HABIs) molecular switches. The light pink color of hexaarylbiimidazole (HABI) in benzene and in polymer films obtained with ultra violet irradiation showed new absorption band at 531 nm. whereas, the light-yellow solution of bridged hexaarylbiimidazole (B-HABI) in benzene quickly turned green under ultra violet irradiation and showed new absorption band at 594 nm. Kinetic study shows that the photodissociation process is faster in B-HABI, and the thermal recombination is faster in HABI. Also, we found that the photodissociation and thermal recombination process decreased with annealing in HABI doped in polymer films. HABI exhibit great stability with 101 repetitive switching cycles in benzene, the absorbance of radical species decreased to 50 % after 97 cycles.

Index Terms— Photochromism, thermochromism, kinetics, fatigue resistance.

I. INTRODUCTION

Nowadays, there are ever growing interest in switching technologies and in the research of development of materials that can be used as switches. In many devices, molecular switching materials have a great applicability as storage [1]-[2], communication elements [3] and as active data elaboration in optical systems for optoelectronics [4], multicolor displays and holographic materials [5]-[6].

Molecular switches can be reversibly shifted between at least two different states, by light energy (photochromism) [7], heat (thermochromism) [8], pressure (piezochromism) [9] and electrical energy (electrochromism) [10]. These two states have different optical properties, emission, redox potential, acid/base strength, dipolar moment, dielectric constant and molecular shape [11]. The most used molecular switching materials in building of photoswitchable smart systems are azobenzenes [12], spiropyrans [13], fulgides [14], diarylethenes [15] and hexaarylbiimidazoles [16]. The photochromism of these photochromic molecules has been employed commercially and it one of the most industrially funded research area [17]. Hayashi and Maeda in 1960 discovered hexaarylbiimidazoles [18], which cleavage to form a pair of 2,4,5-triphenylimidazolyl radicals (TPIR), by light, heat and pressure. Thermal recombination reaction of TPIR to reproduce the original imidazole dimer [19]. In our previous reports multifunctional switches, derived from 9-ethyl-9H-carbazole [20], chlorosubstituted phenyl [21] and piperonal [22] have been discussed and found to have piezochromism, thermochromism and photochromism properties. Based on the photochromism and thermochromism there are several potential switching technologies [23], hence, there is a high motivation to design and study molecular switches. In this paper, we are reporting synthesis of molecular switches of hexaarylbiimidazoles, and study of photochromic behavior in solution and in polymer matrix. Investigation of the temperature-dependent behavior together with the kinetics study.

II. EXPERIMENTAL SECTION

A. Apparatus and chemicals

IR spectra were measured on a Perkin Elmer FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 850 MHz and 400 MHz on a Bruker AVANCE™ III HD, DMSO-d_6 and $CDCl_3$ was used as deuterated solvent. Mass spectra (DART-ToFMS) were measured by using an AccuToF LC-plus JMS – T100LP (Joel) or GCMS on Clarus 560 GC/Mass Spectrometer (PerkinElmer Inc.). UV-Visible spectra were recorded on Evolution 300 spectrometer using 10 mm quartz cuvettes. Melting point were determined with a Stuart Scientific Co. Ltd Apparatus. Commercially available reagents and solvents (from Aldrich Chemical Company, Inc, and ACROS Oraganics) for synthesis were of reagent grade and used without further purification. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm silica gel plates (60F-254).

B. Synthesis of molecular switches

The outline of synthetic procedure of hexaarylbiimidazole (HABI) and bridged hexaarylbiimidazole (B-HABI) is shown in Fig. 1.

Synthesis of 2-(2-chloro-6-fluorophenyl)-4,5-diphenyl-1H-imidazole (3): A solution of 2-chloro-6-fluorobenzaldehyde (1) (12.61 mmol), benzil (2) (12.61 mmol), and ammonium acetate (88.24 mmol) in acetic acid (30 ml) were refluxed in oil bath for 6 h. Then the reaction mixture poured into ice-water and neutralized with sodium bicarbonate. The white precipitate which formed was collected by filtration, washed with water and recrystallized from ethanol to give (3) as white powder. Yield: 94%, m.p.: 81-82 ^{o}C; IR v_{max}/cm^{-1}: 3404 (NH $_{stretch}$), 1571 (NH $_{bend}$), 3057, 2958, 2830 (CH$_{aromatic\ stretch}$), 1669 (C=N), 1603, 1479 (C=C), 1248 (C-N), 1448 (C-F), 897 (C-Cl); ^{1}H NMR (850 MHz, $CDCl_3$, $\square_{ppm}$): 9.464 (s, 1H, NH), 7.983 (d, J = 7.6 Hz, 1H), 7.666 (t, J = 7.0 Hz, 1H), 7.528 (d, J = 7.8 Hz, 1H), 7.511 (d, J = 10 Hz, 4H), 7.336 (t, J = 7 Hz, 4H), 7.145 (t, J = 6 Hz, 2H); ^{13}C NMR (213 MHz, $CDCl_3$, $\square_{ppm}$): 160.62, 137.41, 134.90, 134.65, 132.98, 130.57, 129.92, 129.03, 128.98, 128.26, 127.96, 127.76, 127.00, 126.32, 114.84; MS (GC/MS) m/z: calculated 348.81, found 350.2 (M^{+}+2), 348.2 (M^{+}+1) with a base peak at 165.1.

Synthesis of 2,2'-bis(2-chloro-6-fluorophenyl)-4,4',5,5'-tetraphenyl-2'H-1,2'-biimidazole (HABI): The reaction was carried out in the dark. After dissolution of (3) (7.17 mmol) in benzene (100 ml) in an ice bath, a freshly prepared solution of potassium ferricyanide (28.67 mmol) and potassium hydroxide (86.01 mmol) in 200 ml water was added in a period of 0.5 h at 0 °C and with vigorous stirring. The reaction mixture was stirred overnight at room temperature. The organic layer was collected and washed with water, the water phase was extracted by benzene and combined. The solution was dried over sodium sulfate, evaporated, dried and the resulting solid was recrystallized from benzene/ethanol to give HABI as pale-yellow crystals. Yield: 88%; m.p.: 210-212 ^{o}C; IR v_{max}/cm^{-1}: 3066, 3033, 2923 (CH$_{aromatic\ stretch}$), 1740 (C=N), 1601, 1487 (C=C), 1357 (C-N), 1445 (C-F), 891 (C-Cl); ^{1}H NMR (400 MHz, $CDCl_3$, $\square_{ppm}$): 7.530 (d, J = 6.6 Hz, 4H), 7.495 (d, J = 7.6 Hz, 4H), 7.429-7.350 (m, 8H), 7.119 (t, J = 6.7 Hz, 4H), 7.086 (d, J = 7.0 Hz, 2H), 7.009 (dd, J = 5.7 Hz, 2H), 6.895 (t, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, d_{ppm}): 167.17, 162.79, 160.29, 139.06, 134.39, 131.58, 131.25, 131.13, 131.05, 130.33, 129.76, 129.69, 128.14, 127.91, 127.78, 127.31, 127.28, 126.23, 125.11, 115.53, 115.28; MS (DART-ToFMS) m/z: calculated 695.59, found 697.16 (M^{+}+2), 695.16 (M^{+}+1) with a base peak at 349.09.

Synthesis of 6,6'-([1,1'-biphenyl]-2,2'-diylbis(oxy))bis(2-chlorobenzaldehyde) (5): 2,2'-Biphenol (4) (16.11 mmol), (1) (39.47 mmol) and potassium carbonate (40.28 mmol) were stirred at 100 °C in DMF (50 ml). After 24 h, the reaction mixture was cooled to room temperature and the target compound was extracted with CH_2Cl_2. The organic phase was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated to give a brown powder. The brown powder was purified by column chromatography over silica gel with CH_2Cl_2 as eluent to give a pale-yellow amorphous solid. Yield: 46%; m.p.: 120-122 ^{o}C; IR v_{max}/cm^{-1}: 3078, 3033, 2876 (CH$_{aromatic\ stretch}$), 2777 (C-H, aldehyde), 1697 (C=O), 1585, 1472 (C=C), 1235 (C-O), 925 (C-Cl); ^{1}H NMR (850 MHz, $CDCl_3$, δ_{ppm}): 10.374 (s, 2H, CHO), 7.423 (d, J = 7.7 Hz, 2H), 7.325 (t, J = 7.7 Hz, 2H), 7.268 (t, J = 6.1 Hz, 2H), 7.212-7.193 (m, 2H), 7.050 (d, J = 8.1 Hz, 2H), 6.994 (d, J = 8.2 Hz, 2H), 6.604 (t, J = 7.9 Hz, 2H); ^{13}C NMR (213 MHz, $CDCl_3$, δ_{ppm}): 188.22, 160.28, 152.58, 135.72, 134.15, 132.40, 129.65, 129.37, 125.10, 124.86, 123.51, 120.16, 116.08; MS (DART-ToFMS) m/z: calculated 463.31, found 465.64 (M^{+}+2), 463.61 (M^{+}+1) with a base peak at 307.05.

Synthesis of 2-(2-chloro-6-((2'-(3-chloro-2-(4,5-diphenyl-2H-imidazol-2-yl)phenoxy)-[1,1'-biphenyl]-2-yl)oxy)phenyl)-4,5-diphenyl-1H-imidazole (6): A solution of compounds: (5) (4.32 mmol), (2) (14.96 mmol) and ammonium acetate (64.67 mmol) were stirred at 110 °C in CH_2Cl_2 (5 mL) in a sealed tube. After two days, the reaction mixture was cooled to room temperature and washed with water. The precipitate which formed was collected by filtration and washed with hexane to give a white powder. Yield: 87%; m.p.: 105-107 ^{o}C; IR v_{max}/cm^{-1}: 3410 (NH $_{stretch}$), 1567 (NH $_{bend}$), 3056, 3029 (CH$_{aromatic\ stretch}$), 1631, 1476 (C=C), 1664 (C=N), 1242 (C-N), 1205 (C-O), 919 (C-Cl); ^{1}H NMR (850 MHz, DMSO-d_6, δ_{ppm}): 12.476 (s, 1H, NH), 8.125 (d, J = 9.3 Hz, 4H), 7.913 (d, J = 7.5 Hz, 2H), 7.875 (d, J = 8.3 Hz, 4H), 7.772 (s, 1H),7.673 (t, J = 7.3 Hz, 6H), 7.603-7.577 (m, 4H), 7.497-7.462 (m, 4H), 7.441 (dd, J = 7.7 Hz, 2H), 7.272 (t, J = 7.7 Hz, 2H), 7.204 (t, J = 6 Hz, 2H), 6.942 (d, J = 8.2 Hz, 2H), 6.905 (t, J = 7.4 Hz, 2H); ^{13}C NMR (213 MHz, DMSO-d_6, δ_{ppm}): 159.94, 145.72, 136.55, 136.08, 132.34, 131.70, 131.37, 130.34, 129.71, 129.62, 129.59, 129.51, 129.24, 129.18, 128.99, 128.68, 128.61, 128.31, 128.15, 128.00, 127.90, 127.52, 126.99, 126.94, 126.60; MS (DART-ToFMS) m/z: calculated 843.81, found 846.28 (M^{+}+2) with a base peak at 301.17.

Synthesis of bridged hexaarylbiimidazole (B-HABI): In the dark and under nitrogen, a solution of potassium ferricyanide (118.2 mmol) and potassium hydroxide (238.2 mmol) in water (200 mL) was gradually added during a period of 1.5 h with stirring to a solution of (6) (2.37 mmol) in benzene (200 mL) in an ice bath. The same workup procedure has been followed according to the synthesis of HABI. Recrystallization of the resulting product from benzene/ethanol to give B-HABI as pale-yellow crystals. Yield: 70%; m.p.: 224-226 ^{o}C; IR v_{max}/cm^{-1}: 3058, 3028, 2920 (CH$_{aromatic\ stretch}$), 1590, 1473 (C=C), 1672 (C=N), 1240 (C-O), 1204 (C-N), 917 (C-Cl); ^{1}H NMR (850 MHz, DMSO-d_6, δ_{ppm}): 8.123 (d, J = 7.4 Hz, 8H), 7.684 (t, J = 8.3 Hz, 12 H), 7.592 (d, J = 7.2 Hz, 4H), 7.496-7.461 (m, 4H), 7.450-7.414 (m, 6H); ^{13}C NMR (213 MHz, DMSO-d_6, δ_{ppm}): 159.94, 145.72, 136.55, 132.34, 131.71, 131.37, 129.71, 129.59, 129.51, 129.24, 128.98, 128.92, 128.61, 128.15, 127.00, 126.94, 126.60; MS (DART-ToFMS) m/z: calculated 841.79, found 843.51 (M^++2), 841.12 (M^++1) with a base peak at 300.92.

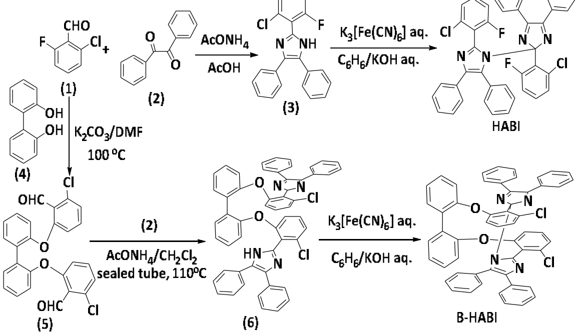

Fig. 1 Synthesis route to HABI and B-HABI

III. RESULTS AND DISCUSSION

C. Switching process

The switching process can be followed by ultra violet-visible absorption spectroscopy. Photochromic HABI underwent photochromic reaction in solution upon irradiation with ultra violet light (UV-light). Colorless solution of photo-dimer in benzene (C_6H_6) quickly turned light pink on irradiation at room temperature, the light pink solution in benzene obtained with irradiation showed new absorption band in the UV region with maxima at 345 nm in addition to absorption band in the visible region ranging from 442 to 580 nm with maxima at 531 nm (Fig. 2). The color gradually reverted to the original color on standing in the dark at room temperature and the absorption band disappear by radical recombination to result in the recovery of the parent dimer. This photochromic behavior is attributed to cleavage of the C-N bond between the two imidazole rings in HABI to give 2-(2-chloro-6-fluorophenyl)-4,5-diphenylimidazole radical (TPIR) (Fig. 3). The absorbance in the visible-region of the radical species was determined after irradiation of benzene solution of HABI in photodissociation process and when kept in darkness in thermal bleaching process (Fig. 4). It is clear from Fig. 4, the photodissociation is slow, HABI reached the photo stationary state after 20 min UV irradiation, whilst the thermal recombination of the radicals was fast, the color faded rapidly in less than 6 min in the dark.

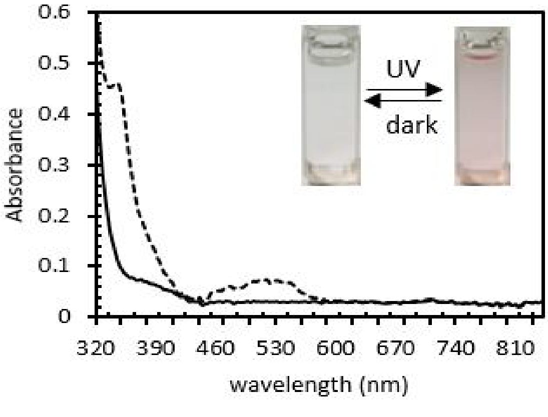

Fig. 2 Absorption spectrum and color changes of HABI in C_6H_6 (10^{-4} M) before UV irradiation (solid line) and after UV irradiation (broken line).

When benzene solution of HABI was heated in a dim light, no changes in color was observed with the rise of temperature. A shoulder at around 383 nm in the UV-region, increased with the rise of temperature, whilst no absorption changes in the visible region (Fig. 5). All attempts to obtain colored radicals of HABI in different solutions with different polarity and concentration up to 10^{-1} M were failed, HABI is not thermochromic.

Photochromic switches have found their advantages commercially with the fast development of polymer industry. The photoproduct formed by photodissociation of the dimer have high photodissociation yield and low sensitivity to the presence of oxygen. The behavior of the photochromic molecules is influenced by the characteristics of the media of the polymer [22]. Poly methylene methacrylate (PMMA) was used to examine the photochromic behavior of HABI in polymer matrix. Three thin films were prepared at various annealing temperature according to general procedure previously reported [24]. The absorption spectrum of unannealed and annealed films of HABI showed no appreciable change before exposing the films to UV irradiation (Fig. 6).

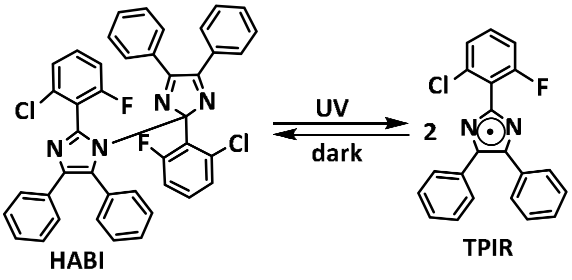

Fig. 3 Photochromic reaction of HABI.

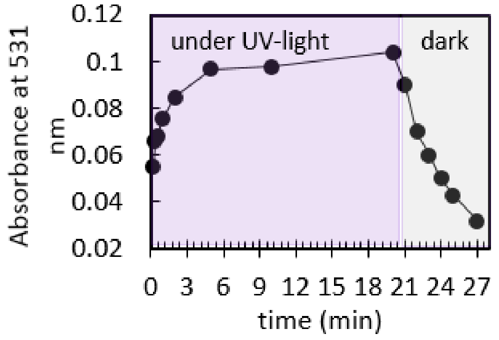

Fig. 4 Absorbance changes at 531 nm of HABI with 365 nm irradiation and thermal fade in the dark in C_6H_6 (10^{-4} M).

The unannealed and annealed thin films of HABI underwent photochromic reaction, the thin films showed new absorption maxima at 531 nm under UV irradiation. We observed that the photocolorability of HABI doped in PMMA thin films is weak. The effect of annealing on the photochromic behavior of HABI is clear from Fig. 7, the absorption of photo product of annealed thin film at 80 °C increases linearly under UV irradiation (Fig. 7a). Whereas, in the dark the absorption of photo product gradually decreased, and the thermal recombination is faster in unannealed film (Fig. 7b).

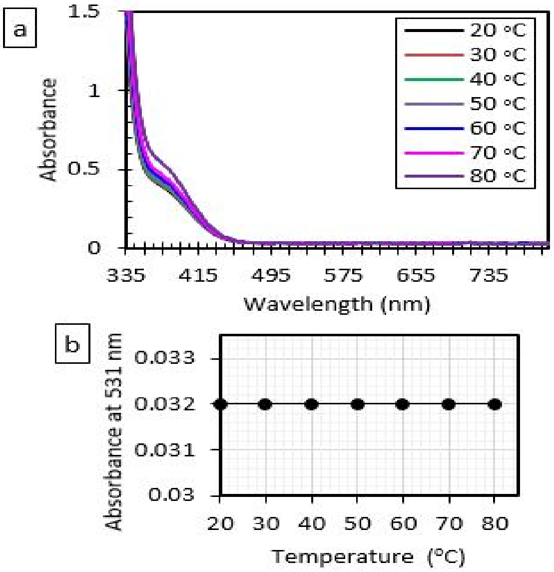

Fig. 5 a) Stacked absorption spectrum and b) absorbance changes at 531 nm of HABI after heating in C_6H_6 (10^{-3} M).

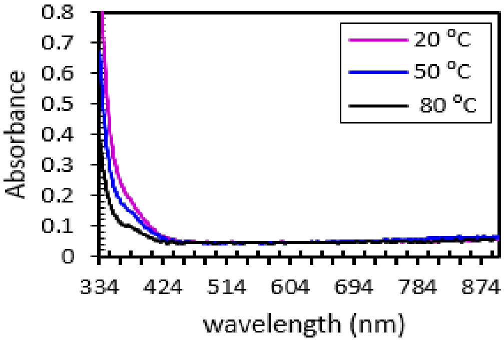

Fig. 6 Absorption spectra of HABI films in dark.

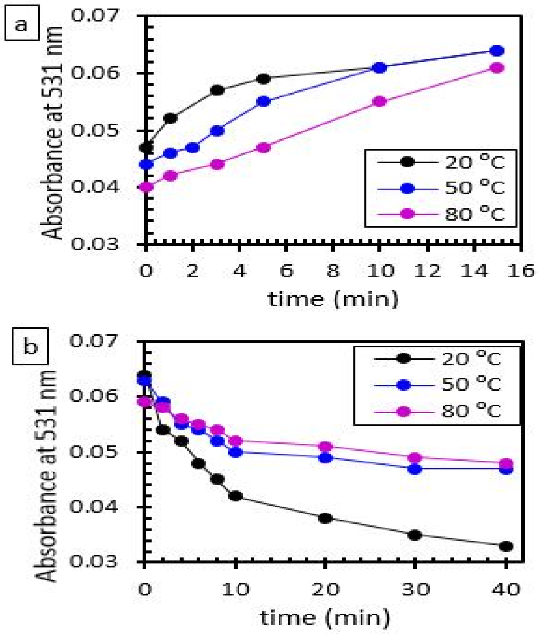

Fig. 7 Absorbance changes at 531 nm of HABI in unannealed film (20 °C), annealed film at 50 °C and annealed film at 80 °C in: a) photodissociation process and b) thermal recombination process.

B-HABI, with biphenyl as a linker to bind the two imidazoles, with chloro groups in the ortho-position of the phenyl rings at the 2-position of the imidazole rings exhibit photochromic properties in solution (Fig. 8). The photocolorability of bridged HABI is low, for this reason, the photochromic reaction was carried out at high concentration. With UV irradiation, the light-yellow solution of bridged dimer in benzene quickly turned green and showed absorption band ranging from 500 to 860 nm with absorption maxima in the visible region at 594 nm (Fig. 9a). UV light breaks the C-N bond between the imidazole rings and the radical pair (B-TPIR) generated. On standing in the dark at room temperature, the new band disappear, the color reverted rapidly to the original color (Fig. 9b), biphenyl bind the two imidazoles rings and prevent the diffusion of the radical pair. The photodissociation of B-HABI is very fast compared to HABI (Fig. 10). B-HABI was heated in different concentrations in benzene, the yellow solution of B-HABI does not showed thermochomic properties. No changes in color was observed with the rise of temperature, however, the absorbance at 594 nm slightly increase at 70-80 °C (Fig. 11).

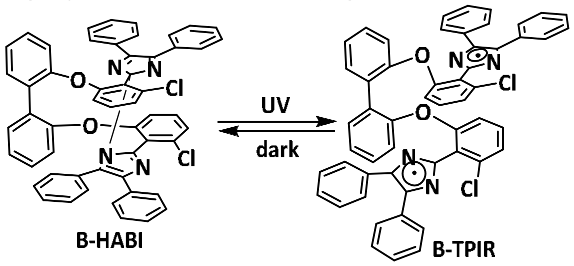

Fig. 8 Photochromic reaction of B-HABI.

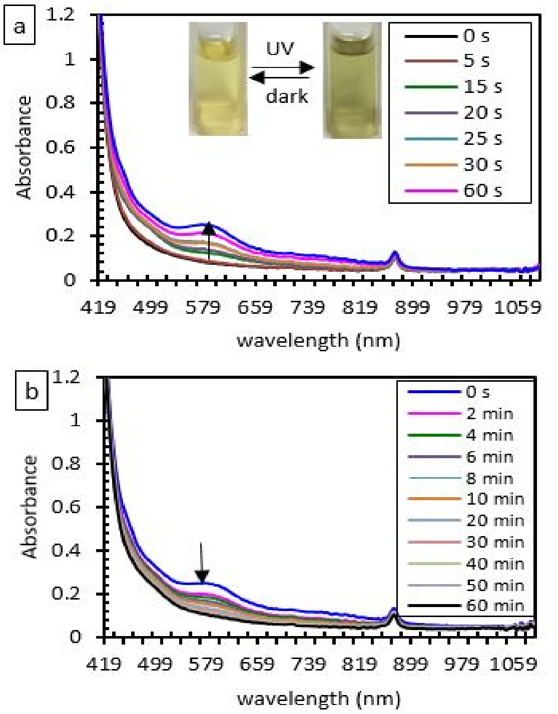

Fig. 9 Stacked absorption spectra and color changes of B-HABI in C_6H_6 (10^{-2} M): a) after 365 nm UV irradiation and b) in darkness.

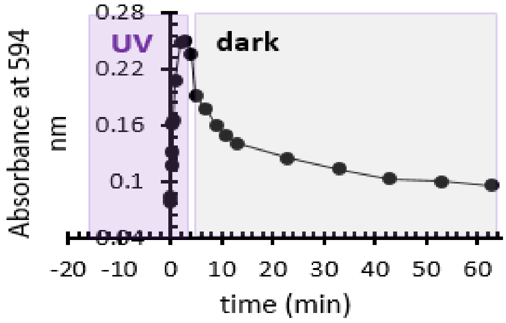

Fig. 10 Absorbance changes at 594 nm of B-HABI under UV light and thermal fade in the dark in C_6H_6 (10^{-2} M).

D. Kinetic measurements

The photodissociation and thermal recombination processes of molecular switches were readily followed spectrally, at measured time intervals, the absorbance at maximum wavelength was determined after irradiation of photochromic solution in photodissociation process and when kept in darkness in thermal recombination process. The photodissociation process and thermal recombination were found to obey first- and second-order rate equations, respectively. The integrated form of the first-order rate law for the photodissociation process is:

$$\ln \frac{A_\infty}{(A_\infty - A_t)} = kt \quad (1)$$

Where k is the rate constant, A_∞ is the absorbance of the radicals at infinite time and A_t is its absorbance at time t. Plot of $[\ln(A_\infty) - \ln(A_\infty - A_t)]$ against time, gives a straight line with slope equals k.

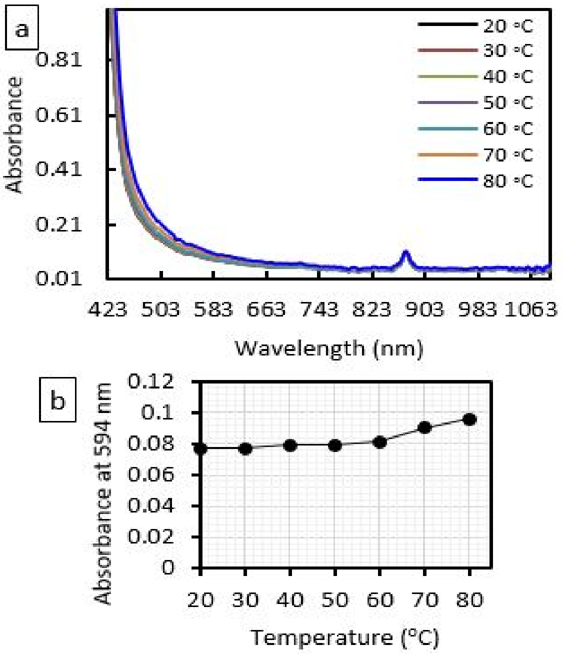

Fig. 11 a) Stacked absorption spectrum and b) absorbance changes at 594 nm of B-HABI after heating in C_6H_6 (10^{-2} M).

In the second-order rate equations, linear plots of $(1/A - 1/A_0)$ versus t were obtained until the absorbance A was about half of the absorbance of the radical species (A_o), when deviations from a second-order plot became apparent.

The kinetic plots of molecular switches in benzene are depicted in Fig. 12, the rate constants and half-lives of molecular switches in benzene in Table 1. In Table 2 the rate constants and half-lives of HABI doped in PMMA polymer films.

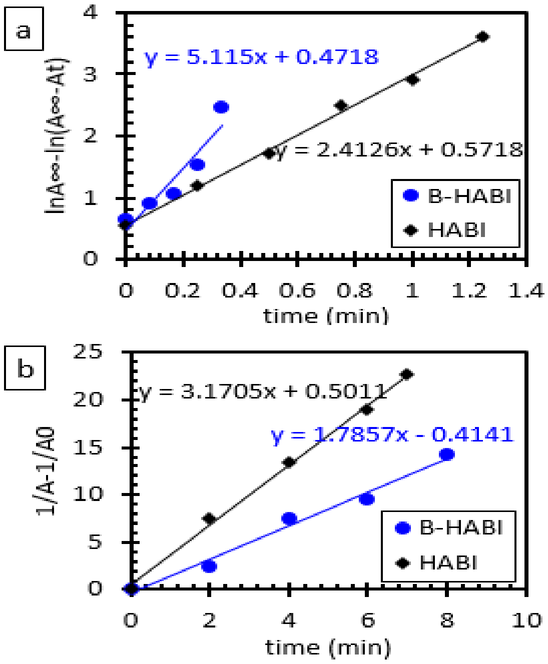

Fig. 12 a) First-order rate plot for the photodissociation process and b) second-order rate plot of thermal recombination process of HABI (c = 10^{-4} M) and B-HABI (c = 10^{-2} M).

Table 1 Rate constants and half-lives for the photodissociation and thermal recombination of molecular switches in solution.

reaction		HABI	B-HABI
photodissociation	K (min^{-1})	241.26×10^{-2}	511.5×10^{-2}
	$t_{½}$ (min)	0.29	0.14
Thermal recombination	K (min^{-1})	317.05×10^{-2}	178.57×10^{-2}
	$t_{½}$ (min)	4.51	8.00

Table 2 Rate constants and half-lives for the photodissociation and thermal recombination of HABI doped in PMMA polymer films at various annealing temperature.

	photodissociation		Thermal recombination	
	k (min^{-1})	$t_{½}$ (min)	k (min^{-1})	$t_{½}$ (min)
20 ºC	16.78×10^{-2}	4.13	76.62×10^{-2}	20.39
50 ºC	16.32×10^{-2}	4.25	39.74×10^{-2}	39.94
80 ºC	12.43×10^{-2}	5.58	22.23×10^{-2}	76.24

It is of interest to extract some remarks from Table 1 and Table 2: In benzene solution, the rate constant is higher in B-HABI and the photodissociation process is faster, whereas, the thermal recombination is faster in HABI. The photodissociation of HABI in benzene solution is faster than in PMMA polymer films due to restriction of the molecular motion in polymer environment [25]-[26].

The photodissociation process of unannealed film of HABI is faster than those of annealed films, photodissociation process decreased with annealing. Also, the thermal recombination of radical species of HABI of unannealed film is faster than those of annealed films. The thermal recombination decreased with annealing.

E. Fatigue resistance

The photochromic molecule to work as a switch should be able to undergo a large number of coloration and bleaching cycles. By irradiation of benzene containing HABI for 2 min and then the radicals kept in darkness for 10 min as one cycle, HABI exhibit great stability, 47.8% nondecomposed of HABI after 101 repetitive switching cycles (Fig. 13a), the absorbance decreased to 50 % after 97 cycles. However, a solution of B-HABI irradiated with UV light for 3 min then faded in darkness for 10 min as one cycle, showed 12 switching cycles, 42% nondecomposed of B-HABI, B-HABI show excellent resistance to fatigue only in 5 repetitive switching cycles (Fig. 13b), the absorbance decreased to 50 % after 10 cycles.

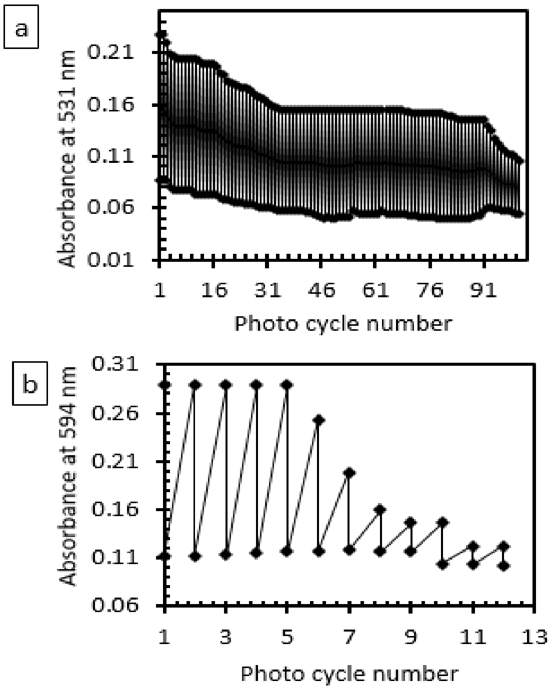

Fig. 13 Switching cycles of: a) HABI monitored at 531 nm and b) B-HABI monitored at 594 nm.

CONCLUSION

Based on the photochromism and thermochromism there are several potential switching technologies, hence, there is a high motivation to design and study molecular switches. To ensure the recycling of the molecular switche, the photochromic system should be photostable and have resistance to fatigue except for some disposable applications, for example, security labels. In this paper we are reporting the synthesis of highly photostable HABI which undergo 101 repetitive switching cycles and B-HABI photoswitch which is most prone to photodecomposition and after 12 switching cycles 42% of the molecule is decomposed.

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