PHOTO-ISOMERIZATION STUDIES OF PARA-SUBSTITUTED ARYLAZOPYRAZOLE PHOTOSWITCHES

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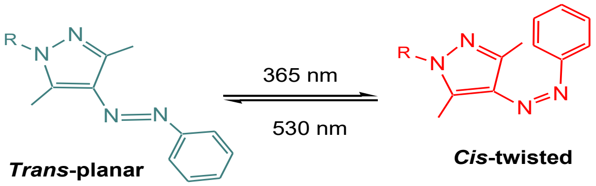
Abstract

Light-responsive molecular switches are powerful tools for controlling chemical and physical processes with high spatial and temporal precision. Among these systems, arylazopyrazoles (**AAPs**) have emerged as an advanced class of photoswitches that exhibit superior photochemical performance compared to traditional azobenzene derivatives that include high thermal stability of the cis-isomer, and near-quantitative photoconversion between isomeric states. This work examines the synthesis and photoswitching behavior studies of para-bromo (**4-Br-AAP**) and 1,8-naphthalimide (**NI**) functionalized arylazopyrazole (**NI-AAP**) based molecular switches. The reversible photo-isomerization properties of the new compounds were characterized by UV–vis absorption spectroscopy. The results show that both the bromo and **NI** substituted small molecular switches exhibit efficient reversible trans-to-cis isomerization upon alternating irradiation with UV (λ = 365 nm) and green (λ = 530 nm). Additionally, the **NI** substituted compound displays a significant blue shift upon light-triggered reversible isomerization. These initial findings establish clear structure–optical property relationships and confirm the suitability of **AAP**-based systems as tunable, high-performance molecular photoswitches for advanced photochemical and materials applications.

Introduction

The development of effective technologies that harvest, store, and convert solar energy is of significant current research interest in renewable energy studies. More recently, molecular photo-switches that undergo photoinduced reversible solid-to-liquid phase transitions (RSLPT) are receiving increasing attention as molecular solar thermal (MOST) energy storage systems.[1-9] In the charging process, a stable *trans*-isomer of these photo-switches absorbs photo energy and is converted to a high-energy metastable *cis*-isomer, thereby storing energy in chemical bonds (**Figure 1**). In the reverse *cis*-to-*trans* isomerization, the energy stored is then released as heat on demand when the metastable isomer is reverted to the stable *trans*-isomer *via* thermal, light, activation. The entire *trans*-to-*cis* and *cis*-to-*trans* isomerization processes provides a closed-cycle solar thermal-energy system that is clean, emission-free, and low cost (**Figure 1**).



To date, azo-switches based materials that store solar energy have been reported.[1-12] Among these arylazopyrazoles (**AAPs**) have been recently introduced as improved light-responsive molecular switches compared to their azobenzene counterpart.[10-12] These heterocyclic azo compounds represent an emerging new class of photo- switches with redshifted wavelength, long thermal half-lives, facile synthetic access and near quantitative *trans*-to-*cis* isomerization in both directions upon irradiation with UV and/or green light, respectively. The substitution of one of the benzene rings from the conventional azobenzene class with a five-membered hetero-aromatic ring leads to a large separation of the π-π^* and n-π^* absorbance of the molecules to enable optimized photochromic behavior.[13-17] This large separation enables the selective isomerization of both isomers with high efficiency to complete *cis*-to-*trans* photo-conversion. These favorable features of the **AAPs** provide great opportunities to design and develop novel MOST materials with long-thermal stability and high energy storage capacity.

The main goal of this research is to design and synthesize new **AAPs** based photo-switchable materials for energy storage and sensing applications. Towards, this goal, in this work, the successful design and characterization of 1,8-naphthalimide (**NI**) functionalized **AAPs** based photo-switchable systems are described. The core design strategy of our study focuses on the incorporation of **AAP** unit into the structure of the Due to their unique photophysical fluorescence attributes and facile synthetic structural modification, 1,8-naphthalimide derivatives have been recognized as fluorophore molecules of choice for the development of fluorescent sensors.[18-20] Furthermore, modifying the structure and conjugation of the NI fluorophore provides a unique opportunity to extend the response wavelength of the molecular switches to visible and even near infrared (NIR) regions. However, although numerous **AAPs** based photo-switches have been reported, to the best of our knowledge, their potential for the design of switchable fluorescent sensors has not been reported.

Experimental Section

Materials and Methods

All chemicals were purchased from commercial sources and used without further purification. All UV-Vis absorption spectra were recorded on an Agilent Cary BIO-60 spectrometer. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrometer. ^{1}H- and ^{13}C-NMR spectra were obtained on a JOEL 400 MHz spectrometer using solvent resonances as internal references.

Experimental Procedure

Synthesis of 4-(bromo)-3-(2-phenylhydrazono)pentane-2,4-dione (2a)

The synthesis of **2a** was carried out following procedures described in the literature.[13] A solution of 4-bromoaniline (1.27 g, 7.4 mmol) was prepared in acetic acid (CH_3CO_2H) (10 mL) and concentrated hydrochloric acid (Coc. HCl) (1.7 mL) in a round bottom flask. Then, a solution of sodium nitrite ($NaNO_2$) (0.610 g, 8.84 mmol) dissolved in H_2O (2.5 mL) at 0 °C was added dropwise. The reaction mixture was allowed to stir for 1 h. Meanwhile, a solution of pentane-2,4-dione (0.98 mL, 9.8 mmol) and sodium acetate ($NaCH_3CO_2$) (1.81 g, 22.06 mmol) in ethanol (7 mL) and water (4 mL) was prepared. After 1 h, the reaction mixture containing the in situ-formed diazonium salt was transferred to the newly prepared solution of the pentan-2,4-dione. The mixture was stirred for another 1–3 h at room temperature. After completion of the reaction, the orange precipitate formed was separated by filtration and washed with ethanol and water (1:1), followed by hexane and air dried.

Orange solid; yield (1.7 g, 93%; 2a). ^{1}H-NMR (400 MHz, $CDCl_3$), (δ ppm): δ: 14.80 (s, 1H), 7.36 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 2.50 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): δ: 198.0, 197.1, 139.2, 136.2, 133.2, 128.1, 116.9, 26.7, 16.4.

Synthesis of 4-Bromo-3,5-dimethyl-(4-phenyldiazenyl)-N-methyl-Pyrazole (3a)

The para-bromo functionalized **AAP** moiety was prepared following methods developed in our laboratory and procedures reported in the literature.[13,17] To a solution of 4-(bromo)-3-(2-phenylhydrazono)pentane-2,4-dione (**2a**) (1.13 g, 4.00 mmol) in ethanol (50 mL), methylhydrazine (0.276 g, 6.0 mmol) was added, and the reaction mixture was allowed to reflux for 5 h in an oil bath. After completion of the reaction, the solvent was evaporated under reduced pressure, yielding 0.85 g of a yellow solid (86%).

Yellow solid; yield (1.80 g, 86%; **3a**). ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): (δ ppm): δ: 7.75 (d, J = 7.6 Hz, 2H, Ar-H, Azo), 7.73 (d, J = 8.5 Hz, 2H, Ar-H, Azo), 4.48 (t, J = 7.3 Hz, 2H, CH_2-O), 4.00 (t, J = 7.2 Hz, 2H, -NCH_2), 3.79 (s, 3H, N-CH_3), 2.58 (t, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): δ: 150.9, 140.5, 134.60, 126.2 (2C), 122.2 (2C), 42.30, 15.5, 12.1.

Synthesis of 4-N-[2-oxoethyl]-1,8-naphthalimide-3,5-(4-phenyldiazenyl)-N-methyl-pyrazole (NI-AAP)

The precursor compound, N-[2-hydroxyethyl]-1,8-naphthalimide, was synthesized following methods developed in our laboratory and procedures reported in the literature.[18-20] To a solution of 4-(bromo)-3,5-dimethyl-N-methyl-pyrazole (**3a**) (1.17 g, 4.0 mmol) in dry acetonitrile (50 mL), potassium carbonate (K_2CO_3) (1.66 g, 3 eq) and 4-bromo-N-[2-hydroxyethyl]-1,8-naphthalimide (1.25 g,1.3 eq) were added and the reaction mixture was allowed to reflux for 24 h in an oil bath. After completion of the reaction, the solvent was evaporated under reduced pressure, affording the desired product (**NI-AAP**) as a orange solid.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.61 (d, J = 6.9 Hz, 2H, Ar-H), 8.23 (d, J = 8.1 Hz, 2H, Ar-H), 7.76 (t, J = 7.4 Hz, 2H, Ar-H),7.76 (t, J = 7.4 Hz, 2H, Ar-H), 7.65 (d, J = 7.8 Hz, 2H, Ar-H, Azo), 7.57 (d, J = 8.7 Hz, 2H, Ar-H, Azo), 4.47 (t, J = 7.3 Hz, 2H, CH_2-O), 3.99 (t, J = 7.2 Hz, 2H, -NCH_2), 3.78 (s, 3H, N-CH_3), 2.56 (t, 3H), 2.47 (s, 3H). ^{13}C NMR (CDCl3, 100 MHz) δ 168.7, 167.6, 165.1, 153.9, 147.7, 141.5, 140.2 137.7, 134.2, 131.5, 128.2, 126.9,122.4, 116.4, 111.6, 61.7, 50.2, 42.8, 13.8, 9.3.

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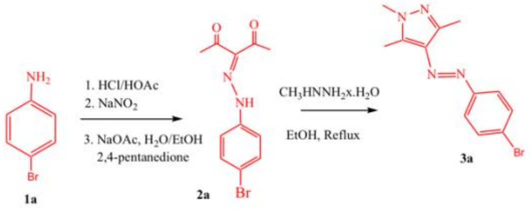
Results and Discussion

Synthesis of 4-(bromo)-3-(2-phenylhydrazono)pentane-2,4-dione (2a)

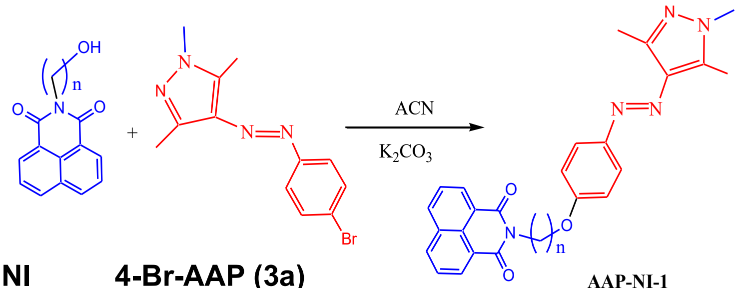
The 4-bromo-3,5-dimethyl-(4-phenyldiazenyl)-N-methyl-Pyrazole (**3a**) derivative was synthesized using 4-bromoanline in two simple steps as described in Scheme 1. In step 1, the 4-bromoanline (**1a**) derivative was converted into a diazonium salt by hydrochloric acid and sodium nitrite, which was subsequently reacted in situ with 2,4-pentandione to afford the precursor hydrazone (**2a**) as a yellow solid in high yield. In step 2, the resulting hydrazone was reacted with methylhydrazine under reflux conditions affording the corresponding 4-Bromo-3,5-dimethyl-(4-phenyldiazenyl)-N-methyl-Pyrazole molecular switch (**3a**) in good yield. Details of the synthesis and analysis of all the compound (**3a**) are provided in the experimental section. The structural characterization of all the intermediate compounds and the final product was carried out using ^{1}H-NMR and ^{13}C-NMR spectroscopy. The NMR results confirm that molecular switch (**3a**) exist in its more stable trans-isomer under normal conditions. This was confirmed by the characteristic pyrazole CH_3 singlet signals resonating in the 2.50–2.60 ppm range in the NMR spectra. See experimental part for details.

Scheme 1: Synthetic route for the 1,8-naphthalimide functionalized arylazopyrazole compound (**3a**).



Design and Synthesis of 1,8-Naphthalimide Functionalized Arylazopyrazoles

The synthesis of the 1,8-naphthalimde functionalized arylazopyrazole molecular photo-switches was carried out by coupling 4-Bromo-3,5-dimethyl-(4-phenyldiazenyl)-N-methyl-pyrazole (**3a**) with N-[2-hydroxyethyl]-1,8-naphthalimide through substitution reaction using K_2CO_3 as a base in refluxing acetonitrile in high yield (85%) (Scheme 2).[15] The structural characterization of the final **NI-AAP** product was carried out using ^{1}H-NMR and ^{13}C-NMR spectroscopy. Similar to that of compound **3a**, the NMR spectral data confirm that the molecular switches exist in their more stable trans-isomers under normal conditions. This was confirmed by the characteristic pyrazole CH_3 singlet signals resonating in the 2.47–2.56 ppm range in the NMR spectra. The ^{13}C spectra also shows characteristics signals at 9-13 (CH_3) and 168.7, 167.6 (C=O). See experimental part.



Scheme 2. Synthetic route for the 1, 8-naphthalimide functionalized arylazopyrazole compound (**NI-AAP**).

Absorption and Photo-switching Studies of 4-Br-AAP (3a)

To confirm photo-isomerization properties, the photo-responsive behavior of compound **3a** was initially studied by UV-vis spectroscopy. Before light-irradiation, the absorption spectra of the trans-isomer of **3a** (20 μM) in methanol displayed two absorption peaks at 340 nm and 440 nm, respectively characteristics of the **AAP** arylazo compounds.[13-17] The strong band at 340 nm can be assigned to the π-π* transitions which corresponds to the **AAP** unit in its *trans*-form (**Figure 2a**). The broad low energy band at 440 nm could be attributed to a mixed n-π* character corresponding to the **AAP** moiety.[16] The **3a** photoswitch recovered to its original trans-rich state after green (530 nm) light-irradiation (**Figure 2b**). For both isomerization directions, the sample solutions were irradiated until the photostationary (PSS) states were reached.

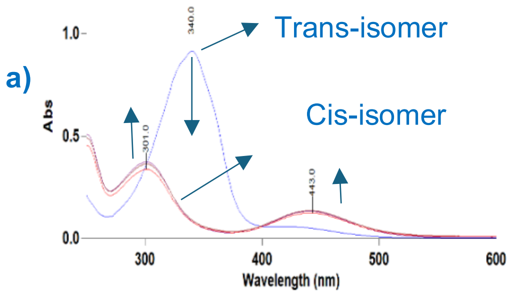


Figure 2. UV-Vis spectra of **AAP-3a**. a) *trans-to-cis* isomerization upon irradiation at λ = 365 nm at 0-20 seconds; b) *cis-to-trans* isomerization upon irradiation with green light λ = 530 nm from 5 min of compounds **3a**.

Absorption and Photo-switching Studies of NI-AAP

The photo-isomerization properties of the 1,8-naphthalimide substituted **NI-AAP** compound was also carried out in a manner similar to that of the **3a** molecular switch. The UV-vis absorption spectra and isomerization study of the **NI-AAP** is shown in **Figure 3**. Like compound **3a**, the photoinduced switching of **NI-AAP** moiety displayed similar absorption spectral peaks at 337 nm for the π-π* and 441 nm for n-π* for the trans-isomer. Irradiation with UV light (λ = 365 nm) led to a shift to lower wavelength and a decrease in intensity for the π-π* transition, while the intensity of the n-π* increases and displays a shift to longer wavelength. This characteristic behavior indicates isomerization from trans-to-cis (**Figure 3a**) leading to the formation of a cis-enriched photo-stationary state (PSS).

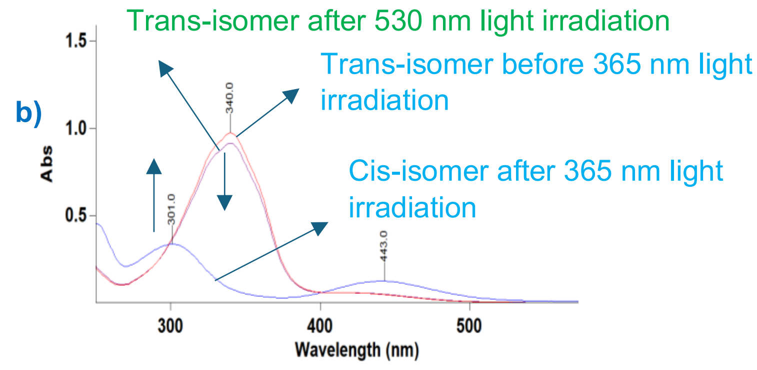
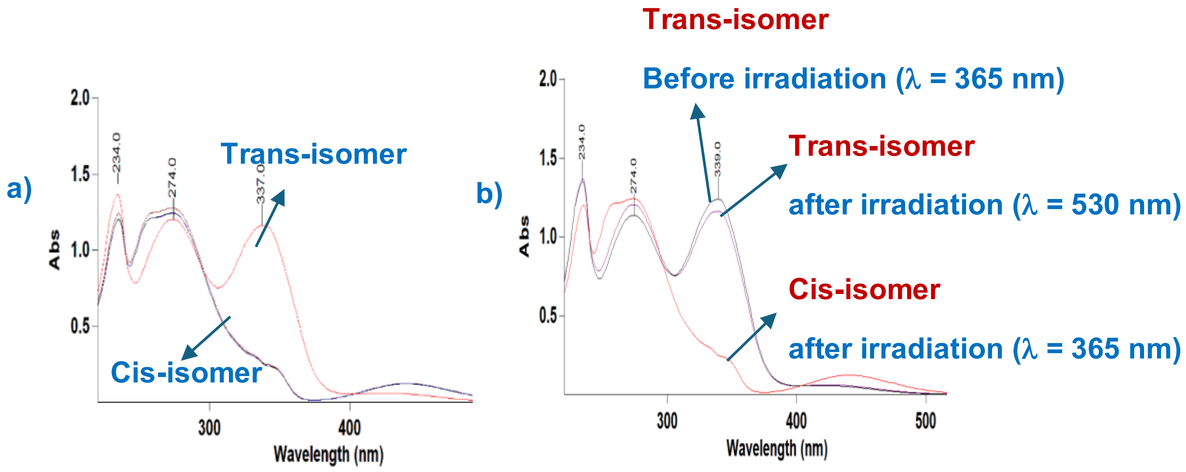
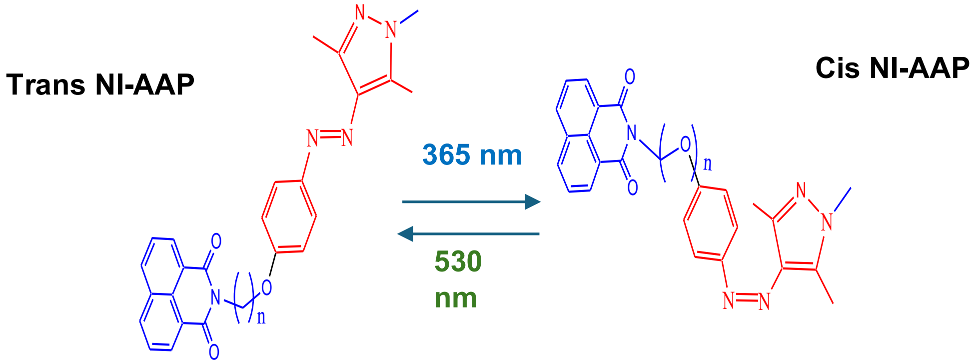


Figure 3. UV-Vis spectra of **NI-AAP**. a) *trans-to-cis* isomerization upon irradiation at λ = 365 nm at 0-120 seconds; b) *cis-to-trans* isomerization upon irradiation with green light λ = 530 nm from 5 min.

Upon irradiation with green (λ = 530 nm), it resulted in a near full recovery of the original spectrum of the **NI-AAP** (**Figure 3b**). These changes indicate that the reversible isomerization of the **NI-AAP** unit can be controlled by light-irradiation in a wavelength dependent manner similar to those other reported arylazopyrazole derivatives.[11-18] Furthermore, the reversibility of the **NI-AAP** was validated by the sequential irradiation at 365 nm and 530 nm and yielded consistent reversible isomerization between the trans-and cis-isomers as quantified by UV-vis spectroscopy (**Figure 3a-b**). For both isomerization directions, the sample solutions were irradiated until the photostationary states were reached. The plausible process for the reversible trans-to-cis isomerization is also described in Scheme 3 below.



Scheme 3. Plausible route for the reversible trans-to-cis isomerization



Conclusion

New photo-switchable bromo and 1,8-napthalimide functionalized arylazopyrazole based molecular switches are synthesized and characterized. The results of the UV-Vis studies indicate that the both the bromo-and 1,8-naphthalimide substituted photo-switches exhibit an efficient reversible *trans*-to-*cis* photo-isomerization upon alternating irradiation with blue and green light. The photo-isomerization of the 1,8-naphthalimide functionalized azo switches also shows more blue shift upon exposure to UV (l = 365 nm) compared to the bromo-substituent. This preliminary data may stimulate further investigation of **AAP** based molecular switches for potential applications in solar thermal energy storage, sensing, photo-pharmacology and coordination chemistry.

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