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# Tuning of Bistability, Thermal Stability of the Metastable States and Application Prospects in the *C*<sub>3</sub> Symmetric Designs of Multiple Azo(hetero)arenes Systems

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#### Dedication ((optional))

**Abstract:** Light-responsive molecular systems with multiple photoswitches in  $C_3$  symmetric designs have enormous application potential. The design part of such molecular systems is critical due to its influence in several properties associated with the photoswitches. In order to tune, and in the evaluation of the design-property relationship, we synthesized 18 tripodal systems with variations in the core, linkers, connectivity, and azo(hetero)arene photoswitches. Through extensive spectroscopic and computational studies, we envisaged the factors controlling near-quantitative photoisomerization in both the directions (bistability) and the thermal stability of the metastable states. Furthermore, we also evaluated the impact of designs in obtaining reversible photo-responsive solgel phase transitions, solvatochromism, photo- and thermochromism.

#### Introduction

One of the recent advancements in the chemistry of azoarenes is the huge impact of systems with multiple photoswitchable units.<sup>[1]</sup> Variations in the linkers and connections of two or more azoarenes in linear<sup>[2]</sup>, branched<sup>[3]</sup>, and cyclic<sup>[4]</sup> fashion were mainstays in this regard. Despite the possibility of several designs utilizing multiple azoarenes,  $C_3$  symmetric systems have been profoundly explored. Indeed, the resulting tripodal designs afforded a wide range of applications such as holographic grating element<sup>[5]</sup>, liquid crystals (LCs)<sup>[6]</sup>, rewritable actuators<sup>[7]</sup> hierarchical supramolecular assembly<sup>[8]</sup>, photoswitchable polymers<sup>[9]</sup>, rewritable image printing and erasing<sup>[10]</sup>, etc. They differ in characteristic features such as molecular size. rigidity/flexibility, groups enabling supramolecular interactions, etc. Ironically, such characteristics influence the properties associated with the azoarenes attached, which has not been fully understood.

It is intriguing to investigate the photoisomerization abilities of individual units to switch between *E*- and *Z*-isomeric states in multiple azoarenes connected systems. Indeed, in *bis*(azobenzene) systems, the relative position of the azo groups (*meta* or *para*) and the extended  $\pi$ -conjugation can influence the electronic coupling between them in the forward isomerization step.<sup>[1a]</sup> However, such electronic conjugation can be decoupled by steric factors.<sup>[2a]</sup> On the other hand, connection of

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unsymmetrical azoarenes that can isomerize at different wavelengths of light leads to multistate (or orthogonal) photoswitching.<sup>[11]</sup> Such systems in principle, exhibit photoswitching over  $2^n$  states, where n = 2, 3, 4, etc., is the number of unsymmetrical azoarenes. Alternatively, macrocyclic ring strain can also dictate such phenomenon.[4e] The concepts of multistate photoswitching are quite advantageous in designing smart materials, optomechanics, and optoelectronic devices.<sup>[12]</sup> Conversely, certain applications like energy storage devices and catalysis necessitate quantitative end-to-end photoswitching without much involvement of the intermediate states, that is, bistability.<sup>[13]</sup> On demand, a C<sub>3</sub> symmetric system with three identical azoarenes can be expected to vield high percentage ZZZ- and EEE-isomers (among the four possible EEE-, EEZ-, EZZ- and ZZZ-photoisomers) in forward and reverse isomerization steps, respectively. However, the existence of photostationary conversions.<sup>[3d,6b]</sup> states (PSS) limits such quantitative

Although factors controlling the multistate photoswitching are known to a reasonable extent, the corresponding knowledge in achieving bistability in the systems with two or more azoarenes is highly desirable. Also, unraveling additional characteristics related to the azoarenes such as solubility, concentration dependency, the thermal stability of the photoswitched states, photoswitching stability, wavelength of light for irradiation, etc. are equally pivotal in improving the design. However, systematic studies on such a plethora of factors towards achieving the bistability, and the impact of overall design towards applications are unknown.



**Scheme 1.**  $C_3$  symmetric designs of tripodal targets. (C: (Het)aryl core; Y: Linker; R: Azo(hetero)arene photoswitches)

In this regard, we have chosen 18 different  $C_3$  symmetric photoswitchable systems (Scheme 1). All those target molecules have been designed in such a way that they have the following features: (a) supramolecular assembly through

hydrogen bonding and/or  $\pi$ - $\pi$  stacking;<sup>[3c,8]</sup> (b) steric factors for disassembly through methyl groups at the core, linker or peripheral positions; (c) rigid or flexible connections of azoarenes through different linkers {-C(O)N(H)-, -C(O)N(CH<sub>3</sub>)-, -N(H)-, -C(H<sub>2</sub>)-, -C(H<sub>2</sub>)N(H)-}; (d) position of the azo group relative to the linker (*ortho, meta,* and *para*) in tuning the electronic coupling; (e) difference in the core units (benzene vs triazine); (f) introduction of azoheteroarene photoswitches owing to their improved photoswitching efficiency, the remarkable thermal stability of the *Z*-isomer, and also increasing application potential,<sup>[14]</sup> and (g) the orientation of the heterocycle moieties.

Through these investigations, we synthesized and characterized the 18 tripodal targets successfully and subjected them to extensive spectroscopic and computational studies. Except **1c** the remaining 17 targets are reported for the first time. Herein, we summarise the outcomes of those studies, in particular, tuning of photoswitching behavior, understanding the thermal stability of the metastable states, and potential application prospects through the factors associated with the designs. Based on these studies, we have also identified the best tripodal  $C_3$  symmetric system exhibiting bistability.



Scheme 2. Synthesis of the target molecules 1-8: (i) SOCl<sub>2</sub>, cat. DMF, reflux, 4-5 h or PCl<sub>5</sub>, toluene, reflux, 4-5 h; (ii) 10, 11a-c, Et<sub>3</sub>N, DCE, rt, overnight, 1a-60%; 1b-75%; 1c-80%; (iii) 10, 12a-c, Et<sub>3</sub>N, DCE, rt, overnight, 2a- 62%, 2b-70%, 2c-72%; (iv) 10, 13a-c, pyridine, toluene, reflux, 4-5 h, 3a-67%, 3b-75%, 3c-85%; (v) 10, 14a-c, Et<sub>3</sub>N, DCE, rt, overnight, 4a-33%, 4b-68%, 4c-20%; (vi) 16, 11a-c, glacial CH<sub>3</sub>COOH, 60 °C, 30 min, 5a-55%, 5b-62%, 5c-65%; (vii) 17a, 15, NaH, CH<sub>3</sub>CN, reflux, overnight, 6-63%; (vii) 17b, 15, Et<sub>3</sub>N, DCE, rt, overnight, 7-70%; (ix) 17a, 11c, K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN, reflux, overnight, 8-62%.

#### Results and Discussion

**Synthesis:** We have synthesized all the 18 tripodal targets using the procedures adopted from the literature (Scheme 2). For accessing the amide derivatives **1a-c** and **2a-c**, their corresponding amino azobenzenes (**11a-c**) or the *N*-methylated aminoazobenzene analogs (**12a-c**) have been treated with the *in situ* generated trimesoylchloride **10**, derived from trimesic acid **9**.<sup>[3c,10,15]</sup> In a similar procedure, **3a-c** and **4a-c** have been synthesized using the corresponding amine derivatives or their *N*-methylated analogs of phenylazo-3,5-dimethylisoxazoles (**13a-c** and **14a-c**).<sup>[6b,14c]</sup> For the synthesis of triazine derivatives **5a-c**, aromatic nucleophilic substitution has been exploited using the corresponding aminoazobenzene derivatives **11a-c** and cyanuric chloride **16**.<sup>[16]</sup> The targets **6** and **7** have been synthesized through a nucleophilic substitution strategy under

basic condition using phenylazo-1*H*-3,5-dimethylpyrazole **15** with 1,3,5-tris(bromomethyl)benzene **17a**, and 1,3,5-tris(bromomethyl)mesitylene **17b**, respectively.<sup>[17a]</sup> Similarly, the target **8** has been synthesized using 4-aminoazobenzene **11c** and 1,3,5-tris(bromomethyl)benzene **17a** using K<sub>2</sub>CO<sub>3</sub>.<sup>[17b]</sup>

Electronic spectral data and photochemical aspects: Foremost, we carried out UV-Vis spectroscopic studies for all the 18 tripodal targets 1-8. Due to the azo chromophores, all the targets in their native state (*EEE*) exhibited a strong  $\pi - \pi^*$ absorption bands (Figure 1 and supporting Section S3). Also, the spectral data revealed that  $n\!-\!\pi^{\star}$  absorption feature was silent except in the cases of 1b, 2a, 2c, 5a, 6, and 7. Apart from the contributions from the linkers through electronic effects, the shifts in the  $\lambda_{max}$  corresponding to the  $\pi - \pi^*$  band signify the extent of  $\pi$ -conjugation. The targets with an azo group at a *para* position relative to the linker units have the maximum bathochromic shift, followed by ortho and then meta. For targets with flexible connections, such as 6, 7, and 8 the  $\pi-\pi^*$ absorption features were observed at 338, 342, and 413 nm, respectively. Compared to these  $\lambda_{\text{max}}$  values, the corresponding simple photoswitches, N-methyl phenylazo-3,5-dimethylpyrazole, and 4-(N-methylamino)azobenzene absorb at 339 and 416 nm, respectively (see supporting Tables S3-1, and S3-2). This indicates that the flexible linkers have a weak influence on the photoswitches. Accordingly, those targets behave like three independent photoswitches despite connected together. The electronic effect arising due to the donating power of the amine linker in 8 leads to the overlapping of  $\pi - \pi^*$  and  $n - \pi^*$  bands (aminoazobenzene type).[18] Compared to benzenetricarboxamide (BTA) derivatives, the corresponding Nmethylated derivatives render a strong blue shift in the  $\pi$ - $\pi^*$ absorption. This is particularly prominent in para derivatives 2c and 4c. On contrast, their ortho and meta analogs 2a,b and 4a,b showed a slight red shift in the  $\lambda_{max}$  relative to the corresponding carboxamides 1a,b, and 3a,b, respectively.

Interestingly, all the targets exhibited high molar absorptivity values indicating very intense  $\pi - \pi^*$  absorption features. Primarily this can be due to the presence of three azo(hetero)arenes. Moreover, this trend is attributable to the substantial localization of the transitions at the azo groups. For the BTA derivatives **1a-c**, and **3a-c**, and their *N*-methylated analogs **2a-c**, and **4a-c**, the  $\varepsilon$  values have no particular dependency on the position of the azo group relative to the linker. However, in the *ortho* derivatives, the  $\varepsilon$  values were found to be lower.

All the derivatives showed good to excellent photoswitching upon irradiation at 365 nm. However, in the cases of 5c and 8, effective isomerization took place at 405 nm owing to red shifted  $\pi - \pi^*$  band. The photoisomerization of *EEE*-isomers exhibited strong spectral changes accompanying the formation of the three potential photoisomers, EEZ, EZZ, and ZZZ. Since these isomeric species are indistinguishable based on the absorption features, the exact composition is impossible to quantify by using UV-vis spectroscopy. Apart from that, we observed an overlap of the  $\pi - \pi^*$  absorption bands of the azo group with that of aromatic moieties upon photoisomerization. This is prominent in the cases of 1a, 2a-c, 4a,b and 5a,b. However, in all those cases, enhancement in the intensity of  $n-\pi^*$  band confirmed the effective photoswitching towards ZZZ-isomer. The  $\lambda_{max}$ corresponding to the  $n-\pi^*$  absorption bands appears in the range between 401 (for 5a) and 446 nm (for 2a). For all the targets, we screened different wavelengths of light to induce the reverse isomerization step towards the native state. Based on the observed spectral changes at their respective PSS, we have also estimated the fraction of molecules underaoina

photoisomerization in the forward and reverse directions (Table S3-1 in the supporting information). Interestingly, in all the three triazine derivatives **5a-c**, we observed an isosbestic point close to the n- $\pi^*$  absorption  $\lambda_{max}$ . This significantly influence the reverse isomerization step causing poor conversion. For selected derivatives **1c**, **2c**, **3c**, **4c**, **5c**, **6**, **7**, and **8**, the fatigue resistance has also been tested up to five cycles. All of them showed excellent reproducibility in the forward and reverse isomerization steps. In order to gain further insights into the electronic spectral data, computations have been performed at DFT level and discussed in a separate section.



**Figure 1.** Representative data on the analysis of photoswitching in **3c**: (a) UV-Vis data depicting the wavelength-dependent photoisomerization in the forward and reverse isomerization sequence (in DMSO, 9.0  $\mu$ M); (b) Photoswitching stability of **3c** over five cycles of forward and reverse isomerization indicating fatigue resistance; (c) Monitoring the thermal reverse isomerization kinetics using UV-Vis spectroscopy (in DMSO, 90 ± 2 °C); (d) The corresponding exponential growth curves of the native state; <sup>1</sup>H-NMR spectral analysis for the estimation of PSS compositions in forward and reverse isomerization (region-wise split, in [D<sub>6</sub>]DMSO, 2.26 mM): (e) before irradiation (*EEE*-isomer); (f) after irradiation at 365 nm/forward isomerization; (g) after irradiation at 490 nm/reverse isomerization (The individual photoisomers of the **3c** are indicated; poor solubility causes low signal to noise ratio in "g").

Table	1.	Es	stimation	of	PSS	con	npositi	on	for
forward	l ar	nd	reverse	ison	nerizat	tion	steps	of	the
selected	l tai	ge	ts using <sup>1</sup>	H-N	MR s	pect	roscop	у	

S. No.	Compound	Conc. (mM)	λ (nm)	%Compo at PSS*	osition of ([D <sub>6</sub> ]DMS	individua O)	I isomers        ZZZ        72        7        86        -        82        74        c        82        -        74        c        82        -			
		( )	(	EEE	EEZ	EZZ	ZZZ			
1	1b⁵	4 16	365	-		28	72			
••		1.10	435	54	27	12	I isomers      ZZZ      72      7      86      -      82      -      74      c      82      -      74      c      82      -      75      90      1      12      -      44      91      2      91      2      91			
2	1c <sup>b</sup>	4 16	365	-	-	14	86			
			450	59	34	7	-			
3	2c°	4 16	365	-	-	18	82			
0.			435	33	57	10	-			
4.	3a <sup>d,e</sup>	1.98	365	-	-	26	74			
			490	С	С	С	С			
5.	3b <sup>b</sup>	2.48	365	-	-	18	82			
			490	41	43	16	-			
6.	3c <sup>b</sup>	2.26 7.79	365	-	3	12	85			
			490	76*	24	-	-			
7.	4b <sup>f</sup>		365	-	-	25	75			
			490	49	36	13	2			
8	4c <sup>f</sup>	4 16	365	-	-	10	90			
0.			490	57	34	8	1			
0	Eal	5.62	365	12	38	38	12			
9	Ja		490	46	40	14	-			
10	509	6.94	405	7	16	33	44			
10.	00-	0.34	490	41	42	17	-			
11	6 <sup>h</sup>	4.16	365	-	-	9	91			
<u> </u>	-		490	55	33	10	2			
12.	<b>7</b> <sup>h</sup>	4 16	365	-	3	6	91			
12.			490	24	33	28	15			

<sup>a</sup>Determined using the normalized integral values of the signals corresponding to the four photoisomers based on the following protons: <sup>b</sup>amide N-H; <sup>c</sup>amide *N*-CH<sub>3</sub>; <sup>d</sup>solubility increased after irradiation at 365 nm; <sup>e</sup>benzene core-H; <sup>f</sup>isoxazole-CH<sub>3</sub>; <sup>g</sup>linker amine -NH-; <sup>h</sup>linker -CH<sub>2</sub>; Wavelength of irradiation: normal – forward; bold – reverse isomerization step (<sup>\*</sup>poor solubility causes lower %*EEE*-isomer in the reverse isomerization step than actual).

Quantification of photoisomers: For understanding bistability, the estimation of the individual photoisomers (PSS composition) for the forward and reverse isomerization steps is necessary. Towards this, we have conducted the photoswitching studies of all the 18 targets in [D<sub>6</sub>]DMSO (at mM concentration). The analysis of the PSS compositions has been carried out using <sup>1</sup>H-NMR spectroscopy (Table 1 and table S4-1 in the supporting information). For the majority of these targets, we identified a non-overlapping proton signal that can exhibit sequential shifts upon isomerization. For each system, the choice of the signal varies between core protons, the methyl protons, the N-H protons depending on the spectral overlap. The broadness and overlapping signals in 2a, 2b, 4a, and 8 hindered quantification of the photoisomers, whereas the solubility issues in the reverse isomerization step did not allow us to estimate the PSS compositions in 1a and 3a. Indeed, 4a exhibited rotamers with many overlapping signals.[19]



Among the systems for which we have obtained the PSS composition in the forward direction, 1c, 2c, 3c, 4c, 6, and 7 showed a maximum conversion of ZZZ isomers in the range of 82-91%. Particularly, the N-methylated derivatives or systems having methyl groups (in the core or the heterocyclic units: 6, and 7, 3a-c, and 4a-c) showed a maximum isomerization. On the other hand, all triazine derivatives 5a-c, and BTA derivatives 1a, and 1b showed a poor isomerization conversion. Although 1c showed a good conversion of about 86% ZZZ-isomer, it displayed a concentration dependency (vide infra). Concerning the position of the azo group, the systems with para connections exhibited excellent isomerization conversions followed by meta connections. Comparatively the systems with ortho connections showed only a moderate isomerization. Presumably the longer wavelength  $\pi - \pi^*$  absorption and extended conjugation play a vital role in effective forward isomerization of para derivatives. This argument is supported by the computed HOMO-LUMO gaps (supporting section S9). The converse holds true for the meta derivates, and so exhibit slightly lower conversions. Whereas, the tautomerism or steric effects are attributed for the poor isomerization conversions in the cases of ortho derivatives. <sup>[18]</sup> The *N*-methylation in the BTA derivatives influences the forward photoswitching only to a marginal extent in the cases of 2a-c and 4a-c. Flexibility enables better forward photoswitching in the case of pyrazole derivatives 6 and 7. Likewise, the estimation of PSS compositions in the reverse isomerization step revealed 1c, 2c, 3c, 4c and 6 as the best photoswitchable systems, however, they exhibit a moderate isomerization conversion towards the native EEE-isomers. Overall, 2c, 3c, 4c, and 6 can be the best tripodal photoswitches in both forward and reverse directions, if EEZ-isomer is also taken into account for the quantification. The weak  $n-\pi^*$  absorption features of the native state limit the complete reverse isomerization under irradiation conditions. The details of the PSS estimation and the data are given (Section S4 in the supporting information).

Solubility and concentration dependency in forward photoisomerization step: Solubility is a crucial parameter for the solution processing of the molecules for various applications and device fabrication. Majority of the targets were found to have a reasonable solubility in different solvents. However, we observed the solubility issues in the cases of BTA or triazine derivatives with the azo groups attached at the ortho position relative to the linkers. In contrast, we observed better solubility for those systems with azo groups connected at meta or para positions. In general, the N-methylation of the carboxamide groups or incorporation of the methylene connections to azoheteroarenes further enhances the solubility. Interestingly, in the cases of 1a, 3a, 3c, and 5a, irradiation at 365 nm (forward photoisomerization) improved the solubility, and on irradiating the solution enriched with the photoisomers at 470 (for 1a) or 490 nm induced precipitation.

Selected targets (those with azo groups connected at *para*position) were tested for concentration dependency in the forward photoisomerization step. Except for the BTA derivative **1c**, and the triazine derivative **5c**, other derivatives showed no or negligible dependency upon varying the concentration up to 10 times. Indeed, Thiele's and Kim's group reported the importance of the concentrations in photoswitching efficiency of **1c**. The possible supramolecular assembly through hydrogen bonding, and  $\pi$ - $\pi$  stacking have been accounted for limiting the isomerization conversions in **1c** and similar systems.<sup>[3c,8b,d,e]</sup> A similar hydrogen bonding between the electron-deficient triazine and N-H linker might be responsible for the concentration dependency in the case of **5c**. Since the supramolecular interactions and assemblies can be hindered through the methyl groups, the other derivatives such as **2c**, **3c**, **4c**, and **6** did not show any effect of concentration on the forward isomerization conversions (Section S5 in the supporting information). Notably, **3c** exhibited no concentration-dependent photoswitching, albeit possessing a BTA core, the moiety capable of forming supramolecular assembly through hydrogen bonding. Probably, the presence of two peripheral methyl groups in the isoxazole moiety either hinders the stacking or induces a weak assembly.

Thermal stability: Apart from the photoswitching characteristics, the stability of the metastable states under ambient conditions is quite significant in the application point of view. In general, a Zisomer of the azoarene can undergo Z-E reverse thermal isomerization through inversion or rotational or concerted inversion or inversion-assisted rotational pathways that depend on substitution, type of azoarene, etc.[18] Thermal barriers and the half-lives associated with the individual metastable states can be tuned by changing the design. Since multiple photoswitchable units containing systems lead to different photoisomers, unraveling the thermal stability of the metastable states involves certain difficulties. This situation is due to the involvement of individual reverse thermal isomerization steps. All our 18 targets contain three photoswitchable groups each, and so the reverse isomerization reactions happen over three consecutive steps, namely, ZZZ-EZZ, EZZ-EEZ, and EEZ-EEE with rate constants  $k_1$ ,  $k_2$  and  $k_3$ , respectively. Indeed, we have investigated the thermal reverse isomerization of the derivatives **1b** and **1c** in [D<sub>6</sub>]DMSO using <sup>1</sup>H-NMR spectroscopy. For understanding the rate-limiting steps, and also to obtain further insights, we performed the reverse thermal isomerization kinetics experiments at variable temperature.

Interestingly, the target 1b showed a slower rate compared to 1c, and so the reaction kinetics was followed at a reasonably higher temperature. Using the composition of the individual isomers at each time interval, we have obtained the time evaluation profiles for both the tripodal systems (Figure 2a,b). By fitting such profiles of each isomerization step, we have estimated the individual rate constants, and the results are tabulated (see supporting Section S6).<sup>[20]</sup> For each step, we have also calculated the activation parameters using Eyring and Arrhenius plots (Table 2). For comparison, transition states have been calculated at B3LYP/6-311G(d,p) and M06-2X/6-311G(d,p) levels of theory through an inversion mechanism for the individual steps (see supporting Section S9). Using these, the corresponding energy barriers associated with all the isomerization steps have also been computed for 1a-c (Table 2, Figure 2c and supporting section S9). Although the trends are quite similar at both the levels of theory, the results obtained at B3LYP/6-311G(d,p) are closer to the estimated activation barriers through experiments.

The comparison of the experimental free energy of activation  $\Delta G^{t}$  in both the molecules revealed that the first step (*ZZZ-EZZ*) is the fastest. Also, the final step (*EEZ-EEE*) is found to be the rate-limiting step. Interestingly, the computed enthalpy of activation  $\Delta H^{t}$  of all the three steps in **1a**, **1b**, and **1c** is nearly the same, whereas they differ only by entropy  $\Delta S^{t}$  contribution. On the other hand, the experimental data revealed that each step has a difference in enthalpy as well as the entropy of activation values. The difference could be arising due to the consideration of gas-phase reaction in the computations, whereas the experiments have been performed in solution phase. Possibly, the dynamics of the photoswitches, steric crowding, and the involvement of solvent interactions can be responsible for it. However, the rate constants k<sub>1</sub>, k<sub>2</sub> and k<sub>3</sub> for

both 1b and 1c exhibited a ratio of almost 3:2:1 confirming the independent nature of the three azobenzene units.<sup>[3c]</sup> Apart from the direct estimation of the activation parameters, we have also estimated the same by including the statistical consideration and the normalized rate constant as described in the literature (see supporting Table S6-2).[2a,3d] Indeed, the normalized rate constants for all the three steps were found to be quite similar. To compare the thermal stability of the metastable states in all the 18 targets, we have deduced the first order formation constants of the native EEE-isomer from their respective photoswitched states. In this regard, we have utilized the UV-Vis spectroscopy and monitored the changes in the absorption corresponding to the  $\lambda_{\text{max}}$  of the  $\pi-\pi^{\star}$  band. Using the exponential growth of EEE-isomer, we estimated the rate constants, and the half-lives (Table 3). Indeed, all the derivatives exhibit higher thermal stability for the photoswitched states at room temperature, and so the isomerization rates were very slow. Hence, we performed the kinetics experiments at elevated temperatures. Interestingly, the rate constants measured by UV-Vis (overall formation rate constant) and <sup>1</sup>H-NMR spectroscopy (the average of normalized rate constants<sup>[2a,3d]</sup> of the individual steps) for **1b** (5.8 x 10<sup>-2</sup> vs 8.3 x 10<sup>-2</sup> min<sup>-1</sup>) and **1c** (1.9 x 10<sup>-2</sup> vs 2.6 x 10<sup>-2</sup> min<sup>-1</sup>) are quite comparable and exhibited a narrow difference. This makes the comparison of the overall formation rates of the other targets quite useful in understanding the trends and also the influence of design part in the thermal stability of the metastable states.

**Table 2.** Experimental activation parameters<sup>a,b</sup> for the thermal reverse isomerization steps and computational data<sup>c</sup>

		Activation parameters <sup>c,d</sup>					
S. No.	Compound	Step	E <sub>a</sub> (kcal mol⁻¹)	∆G <sup>‡</sup> (kcal mol⁻¹)	∆H <sup>‡</sup> (kcal mol⁻¹)	ΔS <sup>‡</sup> (cal mol <sup>-1</sup> K <sup>-</sup> <sup>1</sup> )	
1		ZZZ-EZZ	[22.9]	[20.2]	[23.0]	[2.8]	
2	1a	EZZ-EEZ	[22.9]	[21.2]	[23.0]	[1.1]	
3		EEZ-EEE	[23.2]	[21.9]	[23.2]	[0.4]	
4		ZZZ-EZZ	21.1 ± 0.4 [23.1] (21.7)	24.2 ± 2.4 [20.8] (22.8)	21.1 ± 1.8 [21.9] (21.0)	-12.4 ± 5.5 [1.8] (-6.0)	
5	1b	EZZ-EEZ	22.4 ± 1.1 [23.1] (22.6)	24.2 ± 0.5 [20.5] (22.9)	21.1 ± 0.4 [21.9] (21.9)	-12.4 ± 1.2 [2.3] (-3.5)	
6		EEZ-EEE	22.4 ± 1.1 [23.2] (23.0)	25.5 ± 1.5 [23.0] (23.0)	22.4 ± 1.1 [21.9] (22.3)	-10.4 ± 3.3 [-1.7] (-2.5)	
7		ZZZ-EZZ	19.5 ± 1.9 [22.6] (21.0)	23.0 ± 1.1 [19.9] (21.9)	19.5 ± 0.8 [21.4] (20.4)	-11.6 ± 2.4 [2.6] (-5.0)	
8	1c	EZZ-EEZ	21.4 ± 0.8 [22.6] (22.4)	23.2 ± 0.3 [20.6] (21.7)	20.5 ± 0.2 [21.5] (21.7)	-9.3 ± 0.6 [1.5] (-0.5)	
9		EEZ-EEE	21.4 ± 0.8 [22.7] (23.0)	23.6 ± 0.3 [21.9] (22.8)	20.5 ± 0.2 [21.5] (22.4)	-10.7 ± 0.6 [-0.6] (1.4)	

<sup>a</sup>Estimated by using Arrhenius and Eyring equation through variable temperature kinetics measurements by <sup>1</sup>H-NMR spectroscopy <sup>b</sup>at 298 K. <sup>c</sup>Computed data at B3LYP/6-311G(d,p) level of theory are indicated in the square brackets. All the energies are zero-point energy corrected. <sup>d</sup>The activation parameters deduced using normalized rate constants in kcalmol<sup>-1</sup> ( $E_a$ ,  $\Delta G^t$ , and  $\Delta H^t$ ) and calmol<sup>-1</sup>K<sup>-1</sup> ( $\Delta S^t$ ) are indicated in bold (parentheses) (All the relevant data are available in the supporting information)

	S. No.	Compound	Temp. (°C)	Rate constant (min <sup>-1</sup> )	Half- life (min)	Conc. [µM]
	1	1a	60 ± 2	1.1x10 <sup>-2</sup> ± 3.9x10 <sup>-4</sup>	62	NA
	2	1b <sup>b</sup>	60 ± 2 90 ± 2	5.5x10 <sup>-3</sup> ± 1.4x10 <sup>-4</sup> 5.8x10 <sup>-2</sup> ± 1.4x10 <sup>-4</sup>	126 12	15.3 11.8
	3	1c	60 ± 2	1.9x10 <sup>-2</sup> ± 5.8x10 <sup>-4</sup>	36	10.6
	4	2a	60 ± 2	1.0x10 <sup>-2</sup> ± 4.8x10 <sup>-4</sup>	66	18.7
	5	2b	60 ± 2	4.1x10 <sup>-3</sup> ± 1.0x10 <sup>-4</sup>	168	12.8
	6	2c	60 ± 2	1.3x10 <sup>-2</sup> ±5 .6x10 <sup>-4</sup>	53	14.1
	7	3a	90 ± 2	6.1x10 <sup>-2</sup> ± 2.7x10 <sup>-3</sup>	11	15.7
	8	3b	90 ± 2	2.7x10 <sup>-2</sup> ± 6.8x10 <sup>-4</sup>	26	13.0
	9	3c	90 ± 2	9.4x10 <sup>-2</sup> ± 2.9x10 <sup>-3</sup>	7	9.0
	10	4a	90 ± 2	6.6x10 <sup>-2</sup> ± 4.6x10 <sup>-3</sup>	11	17.9
	11	4b	90 ± 2	2.9x10 <sup>-2</sup> ± 8.1x10 <sup>-4</sup>	24	14.5
Ĺ	12	4c	90 ± 2	4.8x10 <sup>-2</sup> ± 1.1x10 <sup>-3</sup>	14	13.7
	13	5a	60 ± 2	4.2x10 <sup>-2</sup> ± 1.1x10 <sup>-5</sup>	17	10.1
	14	5b	60 ± 2	6.4x10 <sup>-3</sup> ± 3.1x10 <sup>-4</sup>	108	27.6
	15	5c	60 ± 2	4.9x10 <sup>-2</sup> ± 4.1x10 <sup>-3</sup>	14	11.7
	16	6	90 ± 2	3.9x10 <sup>-2</sup> ± 4.8x10 <sup>-4</sup>	18	22.0
	17	7	90 ± 2	4.1x10 <sup>-2</sup> ± 1.0x10 <sup>-3</sup>	17	8.1
	18	8	60 ± 2	1.7x10 <sup>-3</sup> ± 4.4x10 <sup>-5</sup>	6.9	3.5

<sup>a</sup>Rate constants and half-lives corresponding to the overall formation of *EEE*isomer in each case, which was followed by UV-Vis spectroscopy in DMSO at the specified temperature; <sup>b</sup>Additional measurement has been performed at 90  $\pm 2$  °C.

Based on the data, we observed that the systems with *meta* connections of the azo groups relative to the linker units have longer half-lives and higher thermal stability of the photoswitched states. In contrast, those with *ortho* and *para* connections have lower half-lives. As expected, the introduction of azoheteroarenes based photoswitches tremendously improved the thermal stability of the photoswitched states. Overall, the thermal stability of the photoswitched states follows the order: *meta > para > ortho*.<sup>[21]</sup> Significantly, the incorporation of *N*-methylation at the amide nitrogen increases the half-lives in all the cases, whereas the flexibility in the linker or steric factor reduces it.

**Computational studies**<sup>[22]</sup>: To compare the experimental data and in understanding the properties, we subjected all the 18 targets to DFT computations at B3LYP/6-311G(d,p) level of theory. This includes the optimization of each tripodal system in *EEE, EEZ, EZZ,* and *ZZZ*-isomeric states. For gaining further insights, we inspected the HOMO-1, HOMO, and LUMO orbitals for each one of the optimized structures. The molecular orbital analysis revealed that HOMO-1 and HOMO orbitals of the native (*EEE*) isomers of **1a-c**, **2a**, **3a-c**, **4a**, **6**, **7**, and **8** are degenerate, whereas in the cases of **2b**, **2c**, **4b**, and **4c**, they are slightly non-degenerate. But in the case of the triazine-based system **5a-c**, the HOMO-1 and HOMO orbitals for all *EEE*- isomers, except in the cases of **2a** and **4a**, for which the orbitals are  $\pi/n$  mixed.



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**Figure 2.** Representative time evaluation profiles of the thermal reverse isomerization kinetics experiments of (a) **1b** (at 80 °C, in [D<sub>6</sub>]DMSO) and (b) **1c** (at 50 °C, in [D<sub>6</sub>]DMSO) monitored by <sup>1</sup>H-NMR spectroscopy. (c) Computational data (B3LYP/6-311G(d,p) level of theory) on the thermal barriers for the reverse isomerization steps of **1b,c** in terms of  $\Delta G^{\ddagger}$  (in kcal/mol) through inversion mechanism; The relative energies of the photoisomers are also indicated in kcal/mol); (d) HOMO-LUMO gaps (in eV) in the photoisomers of **1a-c**, and (e) Computed electronic absorption spectral data (TD-DFT/6-311G(d,p) level of theory) depicting the changes in the spectral shifts and intensities of the photoisomers in **1a-c**.

On the other hand, the LUMO of all the EEE-isomers corresponds to  $\pi^*$  orbitals. On comparison of the molecular orbitals of ZZZ-isomers of all the targets revealed a mixed  $\pi/n$ nature in both HOMO and LUMO orbitals. Indeed, in all the cases, the non-bonding orbitals corresponding to the azonitrogen are well stabilized and are low-lying. The HOMO-LUMO gap among the ZZZ-isomers revealed that the maximum was for the meta, followed by ortho and then para- isomers (Figure 2d and supporting Figure S9-1). Interestingly, the compounds 5a, and 5b exhibit higher HOMO-LUMO gaps for the photoswitched states rather than the native state with a significant destabilization of the LUMO orbitals. This is corroborating with the observed changes in UV-Vis spectral data. In all the derivatives, the isomerization renders a blue shift along with decrease in the absorption of the  $\pi$ - $\pi$ \* band, whereas in **5a** and 5b, only intensity changes have been observed. To delineate the electronic transitions corresponding to their UV-Vis spectral data, and to shed light into the progressive changes upon photoisomerization, we performed TD-DFT computations for 1a- $\dot{\bm{c}}.$  We observed a blue shift in the  $\lambda_{max}$  corresponding to  $\pi\text{-}\pi^{*}$ transition involving HOMO and LUMO upon isomerization, which is in line with the experimental data. The TD-DFT computations predicted a blue shift for each progressive Z-isomerization step from *EEE*-isomers of  $\pi - \pi^*$  transitions involving the azo group (Figure 2e). Furthermore, the molar absorptivity ( $\boldsymbol{\epsilon}$ ) increases in the order: ortho < meta < para. The  $\varepsilon$ -value decreases drastically as the three-fold symmetry is broken upon isomerization from EEE-EEZ, and drops further in the successive steps. As a result, the ε-value corresponding to ZZZ-isomers were the lowest.

Advantages of the design: The variations in the design provided substantial scope for tuning the photoswitching behaviour and the stability of the metastable states. Also, modifications in the core, linker, photoswitches, the relative orientation of azo groups offered advantages in application perspectives. In this regard, we carefully scrutinized the salient features of each design. The extended conjugation arising due to BTA core results in solubility issues mainly due to the tautomerism in 1a or supramolecular assembly through the combination of hydrogen bonding, and a possible  $\pi-\pi$  stacking in 1b,c. On the introduction of methyl groups at the amide nitrogen, the resulting systems 2a-c exhibited improved solubility and photoswitching. However, the light induced reverse isomerization did not improve. The connection of phenylazo-3,5dimethylisoxazole to BTA core in 3a-c led to an interesting situation, where the supramolecular assembly at the core through hydrogen bonding competes with the steric factor arising due to peripheral methyl groups towards disassembly. As a result, all these systems can be able to exhibit stimuliresponsive sol-gel phase transitions. The most striking aspect is the reversibility in the sol-gel formation in both directions by light. The gel-form in its native state collapsed to sol upon irradiation at 365 nm, whereas it reversed to a partial gel-form by irradiating at 490 nm light (Figure 3a,b and supporting Section S7). Such photoresponsive reversible sol-gel phase transitions have been monitored by polarized optical microscopy (POM). The gel-form of the sample exhibited a birefringence pattern under POM, and upon irradiation at 365 nm light resulted in the sol-form. This can be monitored by the disappearance of birefringence due to the attainment of isotropic phase. The process can be reversed by irradiation at 490 nm light that causes the reappearance of the birefringence. On the other hand, the systems with Nmethylation at BTA cores 4a-c did not exhibit such reversible sol-gel properties at all.

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Figure 3. Evaluation of potential application prospects of various designs of C<sub>3</sub> symmetric tripodal multiple azo(hetero)arenes: Reversible light responsive solgel behaviour in 3c. (a) Gel form in 3c (Formed by using 4.3 mM (0.4 wt%) solution of 3c in a mixture of DMF-H<sub>2</sub>O (3:1) at room temperature) can be converted into sol form by irradiation at 365 nm; this can be reversed to a partial gel by 490 nm irradiation; (b) The corresponding polarized optical microscopic (POM) images for gel and sol forms are depicted (at 10x zoom) (i) Before irradiation; (ii) After 365 nm irradiation (21 s), and (iii) after 490 nm irradiation (523 s); Solvatochromism in 5c: (c) UV-Vis spectral data showing normalized absorptions of 5c in different solvents; (d) Linear relation between the  $\lambda_{max}$  corresponding to the  $\pi-\pi^*$  absorption feature of 5c in different solvents and the hydrogen bond acceptor ability,  $\beta$  (R<sup>2</sup> = 0.84); Photo- and thermochromism in 6: (e) Yellow coloured solid-state and solution phase (in CH<sub>3</sub>CN) samples of 6 in native state; (f) After exposure to a light of wavelength 365 nm exhibiting solid-state and solution phase photochromism; (g) After heating at 90 °C for 30 min (for the solid sample) and 70 °C for 1 h (for solution phase sample) to obtain thermochromism in reversing to the native state; (h) Overall summary depicting the effect of variation in the design of  $C_3$  symmetric tripodal multiple azo(hetero)arene systems and evaluation of key properties (Evaluation scale: ++ = More effective; + = Less effective; 0 = ineffective; x = unknown).

The replacement of benzene core by electron-deficient triazines, and having an amine group as the linker for connecting azobenzenes resulted in the designs **5a-c**. Such systems exhibited longer wavelength absorptions indicating planarity, and/or extended  $\pi$ -conjugation. Apart from that, a potential supramolecular assembly might be responsible for poor solubility,



and concentration-dependent photoswitching. Interestingly, **5c** with a maximum possibility of  $\pi$ -conjugation and the lowest HOMO-LUMO gap exhibited solvatochromism. The  $\lambda_{\text{max}}$  corresponding to the  $\pi$ - $\pi^*$  absorption feature of **5c** exhibited a maximum value of 390 nm in DMSO, whereas it shifted up to 364 nm in chloroform. This trend has a linear correlation with the hydrogen bond acceptor ability ( $\beta$ ) of the various solvents (Figure 3c,d and supporting Section S7).

The flexible connections between photoswitches and the core units make the designs  ${\bf 6},\,{\bf 7},\,{\rm and}\,\,{\bf 8}$  more advantageous. Due to absence of  $\pi$ -conjugation, the photoswitches are the independent. Also, the availability of more room due to the conformational flexibility imparts solid-state photoswitching feasible. We illustrated such solid-state photoswitching using the tripodal system 6 that exhibited a fast switching with a contrasting color change upon irradiation at 365 nm. More importantly, the forward switching can be light-induced (photochromism), whereas the reverse step needs temperature (thermochromism) (Figure 3e-g). Although other designs such as 2a-c, 3a-c, and 4a-c are also capable of such solid-state photoswitching, the color changes and fast switching are characteristics of 6, and 7, which make them useful in the potential applications such as energy storage devices and rewritable image printing. The overall impact of the variations in the design in terms of changes associated with the selected properties of the photoswitches is summarised (Figure 3h).

### Conclusions

Through this investigation, we have systematically designed and synthesized 18 C<sub>3</sub> symmetric tripodal multiple azo(hetero)arenes containing photoswitchable systems. By varying the core, linker, the relative position of the azo group, and the photoswitches, the photoswitching characteristics, and thermal stability of the metastable states have been analysed. Based on the studies, the following key outcomes have been envisaged: (a) Albeit moderate to excellent photoswitching in the majority of the cases, the efficiency in the forward and reverse isomerization lies in the order (based on the orientation of azo group): para > meta > ortho; Among the target systems, **3c** followed by **4c** showed the best photoswitching in both directions. (b) Flexibility allows higher % forward photoswitching, and the systems to behave like three independent photoswitches, however, limits the reverse isomerization; Also, it enables the solid-state photoswitching. (c) The thermal stability of the metastable states strongly depends on the relative position of the azo group and follows the trend: meta > ortho > para. Indeed, the first step is the fastest among the three consecutive isomerization steps, whereas the third step is the rate determining step; (d) The Nmethylation of the amides or the incorporation of azoheteroarenes with methyl groups in the heterocycles improves the solubility, photoswitching efficiency, and also the thermal stability of the metastable states. Through these studies, we also demonstrated that subtle changes in the  $C_3$  symmetric tripodal design can cause a variety of outcomes such as photoand thermochromism, solvatochromism, and reversible photoresponsive sol-gel phase transitions. conclusions will be helpful in These important designing multiple azo(hetero)arenes incorporated systems for a variety of applications.

#### **Conflicts of interest**

There are no conflicts to declare.

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**Keywords:** Azo(hetero)arenes • Multiple photoswitches • Bistability • Sol-gel phase transitions • Photochromism

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- [19] Apart from 4a, the other *N*-methylated amide derivatives 2a-c, and 4b,c also exhibited broadening in the *N*-methyl proton signals. On the other hand, the quantification has been made using the isoxazole methyl proton signals in 4b,c. The data are available as Section S4 in the ESI.
- [20] The kinetics data have been fitted using a program ROOT (version 6.08) available in https://root.cern.ch. The rate constants have been deduced by numerically solving the rate expressions as indicated in the reference 10. The data are available in the ESI.
- [21] In order to understand whether the trend is influenced by the tripodal design or by the position of the azo group relative to the linker alone, we

have synthesized the isomeric benzoyl derivatives of aminoazobenzenes (**Bz-11a-c**). Using these derivatives, photoswitching and reverse thermal isomerization kinetics have been performed. The trends are quite similar to the tripodal designs, which confirms that the position of the azo groups is quite critical for tuning the properties. All the data related to these studies are available in the ESI.

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## Entry for the Table of Contents (Please choose one layout)

Layout 1:

## FULL PAPER

What matters in the photoswitching and thermal stability and application prospects in tripodal photoswitchable systems?



Debapriya Gupta, Ankit Kumar Gaur, Pravesh Kumar, Himanshu Kumar, Anjali Mahadevan, Sudha Devi, Saonli Roy, and Sugumar Venkataramani\*

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Tuning of Bistability, Thermal Stability of the Metastable States and Application Prospects in the C<sub>3</sub> Symmetric Designs of Multiple Azo(hetero)arenes Systems

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