## **Dynamic Architectures on Expanded Heterohelicenes**

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Abstract: Expanded heterohelicenes are an emerging class of heteroatom-containing flexible helicenes, empowered by dual modification with doped heteroatom(s) as well as expanded helicity. Owing to the intriguing fusion of unique structural and electronic features, these molecules captured recent research focus, yielding some fascinating fundamental understanding and new insights in the helicene chemistry, as well as valued electronic and optoelectronic applications. However, limited synthetic strategies to access these molecules act as a major bottleneck for a rapid development of this field by uncovering hidden potentials of purposefully designed taskspecific expanded heterohelicenes. In this regard, expanded heterohelicenes consisting of backbone-decorated dynamic architectures are promising toward exploring stimuli-switchable physicochemical properties and functions; however, they are yet to be developed. In this work, we reported a convenient and modular synthetic protocol for such a novel class of expanded heterohelicenes containing stimuli-responsive core and peripheral modules in order to unearth the hitherto unexplored dynamic properties of these molecules. The rhodium(III)catalyzed method employed here, named as "rollover  $\pi$ -expansion (ROPE)", involves a concurrent linear and angular ring fusions on readily accessible imidazolium-containing pyridines as templates by annulation with alkyne staples, generating a 6-6-5-6-6-6-5-6-6-ring-based expanded polyaza[9]helicene skeleton. The intermediacy of a unique dirhoda-hetero[9]-helicene species generated by quadruple C-H activation-rollover metalation was arrested. Single crystal X-ray crystallographic studies of the dirhoda-hetero[9]-helicene intermediate as well as the expanded polyaza[9]helicenes revealed the origin of the characteristic flexible helical rim and its translation into the organic products. The dynamic behavior of these stimuli-responsive molecules was demonstrated with redox and light triggers, which enabled the molecules to function as reversible hydride-transport and prospective photomechanical molecular spring-like systems.



### Introduction

Helicenes and heterohelicenes are an intriguing class of helically-twisted, angularly-fused polycyclic arenes and heteroarenes respectively, with a unique combination of structural, optical and electronic attributes.<sup>1</sup> Owing to the remarkable properties, these architecturally elegant and aesthetically appealing molecules find rapidly widening applications in both fundamental and applied research domains, ranging from organic synthesis and asymmetric catalysis,<sup>1a</sup> crystal engineering,<sup>2</sup> supramolecular and host-guest recognition,<sup>3</sup> to electronic/optoelectronic/non-linear optical materials and devices,<sup>4</sup> polarized light emission,<sup>5</sup> and chirality-driven biological functions.<sup>6</sup> In contrast to the helicity in the classical helicenes/heterohelicenes stemmed from purely angular ring-fusions, one or more linear fusions along with the angular ones in the helical rim, give rise to a new type of helicity – *expanded helicity* – thus resulting in a novel category of helical molecules termed as *expanded helicenes*<sup>7</sup>/heterohelicenes,<sup>8</sup> featured with increased helical diameter and flexible structure. The expanded helicity with structural flexibility in this class of molecules emerged as an alluring feature which attracted recent

attention by opening up an opportunity to unearth unique or enhanced properties and harness an array of functions. For instance, the expanded [13]helicenes synthesized independently by Tilley<sup>7a</sup> in 2017, and by Hirose and Matsuda<sup>7b</sup> in 2018 showed remarkable long-range  $\pi$ -stacking (a prospective property for charge-transport application) and soft molecular spring-like behaviour, respectively. On the other hand, the expanded heterohelicenes are enabled with dual modification in the form of doped heteroatom(s) as well as expanded helicity, thus expressing tuned properties and special functions (Figure 1). Examples include single-molecule conductivity application (as in I),<sup>8b</sup> high fluorescence quantum yields (as in II),<sup>8c</sup> and multiple resonance thermally activated delayed fluorescence (MR-TADF) emitter in organic light-emitting diode (OLED) devices via enhanced reverse intersystem crossing (RISC) process (as in III),<sup>8d</sup> all discovered very recently during 2017-2022 (Figure 1). As far as the chemistry of expanded heterohelicene is concerned, in contrast to exploring the fixed physicochemical properties with static backbone of the molecules as noted above, one potential advancement in this area would be to manoeuvre their switchable properties with dynamic architectures by introducing stimuliresponsive modules within their backbone. This would make them promising candidates for a range of practical applications in line with the wide utility of switchable molecular materials across different spheres of research fields.<sup>9</sup> However, such enticing type of dynamic expanded heterohelicenes with stimuli-switchable physicochemical properties is yet to be developed. This scarcity might be associated with considerable synthetic challenge involving design of appropriate molecular architectures with befitting components which would respond to stimuli and govern the dynamicity, yet maintaining the expanded helicity. This is in stark contrast to the extensively- developed and widely-investigated stimuli (pH, redox, photo)-responsive classical (nonexpanded) helicenes/heterohelicenes exhibiting, for example, reversible change of chiroptical property.<sup>1e,10</sup>



**Figure 1**. Previous studies: exploring static property of expanded hetereohelicenes; this study: integrating dynamicity into the properties of expanded heterohelicenes.

Exploiting our hybrid knowledge on synthetic protocols toward  $\pi$ -conjugated heteroaromatics via C–H activationalkyne-annulation chemistry,<sup>11</sup> and design of stimuli-switchable molecules,<sup>12</sup> herein, we report the utility of *rollover*  $\pi$ -*expansion* (*RoPE*) approach for ready access of an array of flexible expanded polyazahelicenes featuring stimuli-responsive modules at the core (redox-responsive) and peripheral (light-responsive) backbone, to make use of their dynamic properties (**IV**, Figure 1). This strategy involves a concurrent linear and angular ring fusions on readily accessible imidazolium-containing pyridines as templates by annulating with alkyne staples, generating 6-6-5-6-6-5-6-6-5-6-6-ring-based hetero[9]-helicene skeleton, via the intermediacy of novel dimetalla-hetero[9]helicene species formed by a quadruple C–H activation-rollover metallation process (Scheme 1). We further illustrate the unique structural features, along with photophysical and electronic characteristics of these molecules. Finally, the dynamic behaviour of these stimuli-responsive molecules was demonstrated under the influence of the redox and light triggers, which enabled the molecules to function as reversible hydride-transport and prospective photomechanical molecular spring-like systems.





#### **Results & Discussion**

### Synthetic and Structural Aspects

The RoPE protocol of the 2,6-disubstituted bis-imidazolium-containing pyridine templates Pybim1 and Pybim2 with variable alkynes catalyzed by [Cp\*RhCl<sub>2</sub>]<sub>2</sub> led to the convenient synthesis of the present series of dicationic expanded polyazahelicene molecules ExHHel1–ExHHel5, isolated as racemic mixture of both (P) and (M) isomers (Scheme 1). The proposed quadruple C–H activation-rollover metallation process was arrested by synthesizing one representative intermediate with the template **Pybim1**. A stoichiometric reaction of **Pybim1** and  $[RhCp*Cl_2]_2$ in the presence of NaOAc in 1,2-dichloroethane (DCE) at 120 °C for 36 h provided the intermediate Rh2-ExHHel as a racemic mixture (Scheme 1). It is to emphasize here that the synthesis of five-membered cyclometalated species with large helically-strained aromatic backbones via C-H activation is still a challenging task, because the requirement of the coplanar geometry of the corresponding two sterically-hindered rings of such nonplanar arene substrates, involves high energy barrier during the C-H activation process.<sup>13</sup> Most significantly, the crystallographic analysis revealed a helical structure of Rh2-ExHHel with a molecular diameter of 14.2 Å and helical diameter of 7.4 Å, thus representating a rare bimetallic metallahelicene with two metal-containing rings being part of the contiguous helical network of mixed 'carbocycle-heterocycle-metallacycle' arrangement containing 6-6-5-5-6-5-5-6-6-ring-based [9]-helicene skeleton (Figure 2A,D).<sup>14</sup> The crystal packing of Rh2-ExHHel showed the presence of alternatively stacked *P* and *M* enantiomers together along the vertical direction to form a racemic column structure (Figure 2G). The unsuccessful separation of the helical isomers might be associated with the flexibility of the two helicenic wings to flap up and down with a plausibly low configurational barrier, a typical characteristic of expanded (hetero)helicenes. A large helical pitch (centroid-centroid distance between two terminal overlapping rings, i.e., rings A & I) of 3.84 Å suggested the influence of the two contiguous metallacycle rings having the piano-stool geometry at the metal centre with its ligands, within the helical rim, to move the two terminal rings away from each other, overweighing their  $\pi$ - $\pi$  interactions (Figure 2A). This fact was also supported by the large intersecting angles,  $\vartheta_{AE}$  and  $\vartheta_{IE}$ , both 37.1°, between the terminal rings A or I, and the plane along the central pyridine ring E respectively. However, expectedly, the helical rim still maintained moderate flexibility due to the expanded design, as evident from a low intersecting angle ( $\vartheta_{AI}$ ) of only 5.5° between the two planes passing through the terminal rings, implying that these two rings lie almost parallelly within the helix (Figure 2D).

Next, **Rh**<sub>2</sub>-**ExHHel** was subjected to stoichiometric and catalytic annulation reaction tests with diphenylacetylene as the alkyne (Scheme S8-9, Supporting Information). The successful formation of **ExHHel1** in both experiments certified that **Rh**<sub>2</sub>-**ExHHel** acted as a putative intermediate in the catalytic cycle for the abovementioned *RoPE* reaction. Because, **Rh**<sub>2</sub>-**ExHHel** was an intermediate en route to the products, it is expected that its helical structure eventually induced the helicity into the resulting dicationic expanded heterohelicene product molecules, formed just after the alkyne stapling at the metal sites. Indeed, the translation of the unique flexible helicity and related characteristics present within **Rh**<sub>2</sub>-**ExHHel** into the final products, was clearly evident from the crystal structures, molecular arrangement and packing of the two representative dicationic compounds **ExHHel2** and **ExHHel4**, consisting of a penta-aza[9]-helicenic core with fully-conjugated 6-6-5-6-6-5-6-6-ring arrangement (Figure 2). They also featured a large molecular diameter of approx. 13.3 Å and helical diameter of approx. 7 Å, due to the laterally-expanded helix backbone (Figure 2B,C). The crystal packing of **ExHHel2** and **ExHHel4**, was similar to **Rh**<sub>2</sub>-**ExHHel**, having the alternatively stacked *P* and *M* enantiomers in racemic column structure (Figure 2H,I).



**Figure 2**. Crystal structures and relevant geometrical parameters (A-C), side views of the molecular structures (D-F), and crystal packing showing the arrangement of the *P* and *M* enantiomers (G-I) of **Rh**<sub>2</sub>**ExHHeI**, **ExHHeI2** and **ExHHeI4**. Definitions: helical pitch = centroid-to-centroid distance between the two terminal rings A and I; helical diameter = centroid-to-centroid distance between the two terminal rings A and I; helical diameter = centroid-to-centroid distance between the two rings C and H within the helical rim;  $\vartheta_{AI}$  = intersecting angle between the two planes passing through the terminal rings A and I;  $\vartheta_{AE}$  and  $\vartheta_{IE}$  = intersecting angles between the plane along the central pyridine ring E and the terminal rings A and I respectively; ( $\varphi_{AE}$ ) and ( $\varphi_{IE}$ ) = mean torsion angles at the inner side of the helical rim starting from ring A to ring E and from ring I to ring E respectively. CCDC Nos.: **Rh**<sub>2</sub>**ExHHel1**: 2158814; **ExHHel2**: 2158816; **ExHHel4**: 2158813.

As expected, the racemization barrier values calculated for **ExHHel2** and **ExHHel4** lied within the range of 17-18 kcal/mol at 25 °C (Table S5). The values were comparable with previously reported [7]heliphene ( $\Delta G^{*}_{experimental} = 12.6 \text{ kcal} \cdot \text{mol}^{-1} \text{ at } -27 \text{ °C}$ ),<sup>15</sup> [13]helicene-based helical kekulene analogue ( $\Delta G^{*}_{theory} = 13.0 \text{ kcal} \cdot \text{mol}^{-1} \text{ at } 25 \text{ °C}$ ),<sup>7b</sup> and the aza-bora[9]helicene **II** ( $\Delta G^{*}_{theory} = 14.3 \text{ kcal} \cdot \text{mol}^{-1} \text{ at } 25 \text{ °C}$ ).<sup>8c</sup> Further, the half-life values ( $\tau_{1/2}$ ) of the helical inversion process were  $\tau_{1/2} = 0.4$ , and 2.6 s at 25 °C for **ExHHel2** and **ExHHel4** respectively, suggesting fast kinetics of helical inversion, in accordance with the characteristics of flexible helicene rim. In fact, the increased flexibility in **ExHHel2** and **ExHHel4** as compared to the intermediate **Rh**<sub>2</sub>-**ExHH**, was indicated by relatively smaller (i) helical pitch values of 3.56 Å and 3.48 Å respectively, and (ii) intersecting angles,  $\theta_{AE}$  and  $\theta_{1E}$ , of 22.1° and 21.5° respectively (Figure 2A-C). The small intersecting angle,  $\theta_{AI}$ , of 8.9° and 3.2° for **ExHHel2** and **ExHHel4** respectively, also suggested the maintainance of the flexible helicity within these molecules. In addition, the small values of the mean torsion angles at the inner side of the helical rim of **ExHHel2** and **ExHHel4**, starting from ring A to ring E ( $\varphi_{AE}$ ) (12° and 12.5° respectively) and from ring I to ring E ( $\varphi_{1E}$ ) (11.8° and 12.5° respectively) are also a signature of expanded helicity (Figure 2A-C).

# **Photophysical and Electrochemical Features**

The compounds **ExHHel1**, **ExHHel2**, **ExHHel3** and **ExHHel5** exhibited well-resolved  $\pi$ - $\pi^*$  absorption band around 433–445 nm region along with additional higher energy bands, and an emission band around 570–584 nm region in chloroform (Figure 3A). These absorption bands were ascribed to the HOMO–LUMO (and HOMO-1 to LUMO) transitions as supported by the time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G(d,p) level of theory (Table S7). It was noticed that alkyl or aryl substituents on the periphery had a negligible effect on the absorption or emission spectral shift when compared in a common solvent (e.g., chloroform), indicating limited  $\pi$ -conjugation of the peripheral groups with the helicenic core due to twisted geometry. In contrast, additional  $\pi$ -extension of helicenic core, as present in the pyrene-embedded helicene **ExHHel4**, resulted in red-shifted absorption to 483 nm and emission to 645 nm (Figure 3A), due to efficient  $\pi$ -conjugation. Interestingly, all the compounds **ExHHel1–ExHHel5** showed large Stokes shift (126–162 nm; 4979 cm<sup>-1</sup> to 5200 cm<sup>-1</sup>) in various solvents; the flexibility of the helicenic core and significant structural changes between the ground state and excited state were accountable for considerable Stokes shift values.<sup>1j,16</sup> These dicationic heterohelicenes exhibited quantum yield values in the range of  $\phi = 0.06 - 0.21$  in CHCl<sub>3</sub> (except **ExHHel4**) and the excited-state lifetime values in the range of 2.4–6.2 ns (except **ExHHel4**) in chloroform. Interestingly, some of these compounds display bright emission in solid states also along with the solution state (Figure 3B).

We noticed that the highest occupied molecular orbital (HOMO) of ExHHel1–ExHHel4 was mostly delocalized over the conjugated  $\pi$ -rich phenanthrene or pyrene unit, whereas the lowest unoccupied molecular orbital (LUMO) was delocalized on the dicationic aza-anthracene core of the helicenes (Figure 3C, representative systems). Variantly, in **ExHHeI5**, the HOMO was localized on the thiophene units, but the LUMO distribution was similar to other congeners. Expectedly, in all of these molecules, the LUMO energy was found to be similar, but the HOMO energy was variable (Figure 3D). In case of ExHHel1-ExHHel3, the energy of the HOMO was similar and the influence of the peripheral substituents (aryl/alkyl) was significantly less, which was also reflected on their absorption and emission properties. In contrast, ExHHel4 experienced destabilization of the HOMO ascribed to an increased  $\pi$ -electron cloud on the pyrene unit. Similarly, for **ExHHel5**, electron-rich thiophene units elevated the HOMO energy level. Thus, the HOMO-LUMO energy gap varied in the order of ExHHel1 ~ ExHHel2 ~ ExHHel3 (ca. 2.9 eV) < ExHHel4 ≈ ExHHel5 (ca. 2.5 eV), and well-supported by the experimentally observed order of optical bandgaps (Figure S12). Electrochemically, **ExHHel1–ExHHel5** exhibited a quasi-reversible reduction wave in the range of -0.58 to -0.68 V (vs Ag/AgCl) (in acetonitrile), and irreversible reduction waves were observed within a potential range of -1.02 V to -1.12 V (vs Ag/AgCl) (Figure S13). However, no oxidation waves (except ExHHel5) were found for these molecules up to 2.0 V vs Ag/AgCl (in acetonitrile). This behaviour suggested that removal of electrons from the stabilized HOMO was difficult, whereas electron-injection to the stabilized LUMO residing mainly on the electron-deficient fused bis-imidazolium-based dicationic aza-anthracene core, was easy in these expanded heterohelicenes.



**Figure 3**. (A) Absorption (solid lines) and emission spectra (dotted lines) of **ExHHel1-ExHHel5** in CHCl<sub>3</sub>. (B) Images of emission color from **ExHHel1-ExHHel5** in CHCl<sub>3</sub> (upper panel) and in solid-state (lower panel). (C) Frontier molecular orbital (FMO) diagram of **ExHHel1** (left) and **ExHHel5** (right). (D) HOMO-LUMO energy gaps computed by DFT method (B3LYP/6-31G(d,p) level of theory).

# Reversible Redox-responsive Behavior and Switchable Hydride Storage/Delivery Function

Prompted by the above LUMO features on the core of the helical rim of these expanded heterohelicenes, controlled reduction of the bis-imidazolium-based dicationic aza-anthracene core in **ExHHel1** was conducted with cobaltocene (CoCp<sub>2</sub>) in CH<sub>2</sub>Cl<sub>2</sub> whereupon the color of the reaction solution changed initially from yellow to orange, and then to pink (Figure 4A). The orange-colored solution was subjected to electron paramagnetic (EPR) spectroscopic analysis which suggested the presence of a cation radical, featuring g value of 2.0029 consistent with an organic radical (theoretical g = 2.0023 for a free electron) (Figure 4D). The spectrum showed a broadened line consisting of no signature of hyperfine coupling with the surrounding nitrogen atoms and the hydrogen atom of the central pyridine ring, suggesting extensive delocalization of the radical over the bis-imidazolium-based dicationic aza-anthracene core of the molecule. Indeed, the calculated spin densities supported such extensive spin delocalization thus disallowing any hyperfine interactions to be observed (Figure 4E). A similar orange solution could also be achieved upon reducing the starting material with triethylamine as the single-electron reductant. Interestingly, when the orange solution was quenched by adding water to it, an imidazolium-ring-



**Figure 4.** (A) Reversible redox chemistry of **ExHHel1**. (B) Single crystal X-ray structure of **ExHHel1-CONH** (CCDC No. 2158817). (C) <sup>13</sup>C-DEPT-135 spectrum of the hydride product **ExHHel1-red**. (D) EPR spectrum of the in situ-generated proposed radical cation of **ExHHel1** in CH<sub>2</sub>Cl<sub>2</sub>. (E) Spin density plot of the in situ-generated proposed radical cation **[ExHHel]**.<sup>+</sup> (B3LYP/6-31G(d,p)). (F) Change of absorption spectrum of 10  $\mu$ M **ExHHel1** upon hydride-transfer with NaBH<sub>4</sub> and its reversible regeneration by proton-transfer using HNO<sub>3</sub> in CH<sub>3</sub>CN. (G) Reversibility of hydride-transfer process with **ExHHel1** (10  $\mu$ M in CH<sub>3</sub>CN). The absorbance value at  $\lambda_{max}$  = 550 nm was monitored for switching study upon consecutive addition of NaBH<sub>4</sub> (pink dots) and HNO<sub>3</sub> (green dots).

cleaved product **ExHHel1-CONH** was obtained, as characterized by <sup>1</sup>H NMR spectroscopy, ESI-MS and SCXRD analysis (Figure 4A,B, and SI). The formation of this product suggested that the reactivity was originated from the imidazolium ring-centred radical. Most interestingly, in the absence of water, the cation-radical followed a different course of reactivity originated from the central pyridine ring-cantered radical and was found to abstract hydrogen atom from the solvent ( $CH_2Cl_2$ ), forming a new type of helical organic hydride product **ExHHel1-red**, accompanied by a color change from orange to pink (Figure 4A). The reduced hydride product **ExHHel1-red** was characterized by <sup>1</sup>H, <sup>13</sup>C and DEPT NMR spectroscopy, and ESI-MS studies (Figure 4C and SI). For example, in the <sup>1</sup>H NMR spectrum in  $CD_3CN$ , the appearance of a new singlet peak at 3.74 ppm for **ExHHel1-red** corresponding to the newly formed - $CH_2$  group was evident (see SI) which was further confirmed by <sup>13</sup>C and DEPT-135 NMR analysis (Figure 4C). Therefore, the overall reduction ( $1e^- + H$  atom) of the dicationic **ExHHel1** to the monocationic hydride product **ExHHel1-red**, was achieved by aqueous NaBH<sub>4</sub> solution (a well-known hydride

source), involving similar color-change (directly from yellow to pink) of the solution (Figure 4A,F). The reduced product ExHHel1-red formed in this reaction was also verified independently by NMR spectroscopy and was found to be the same one as obtained in the previous method. Although a single crystal of **ExHHel1-red** suitable for Xray diffraction could not be obtained after several attempts, it is important to mention here that we prepared a similar model compound (Mod-red) by NaBH<sub>4</sub> treatment of the corresponding cationic precursor and succeeded to obtain crystal structure of it which unambiguously confirmed the hydride structure as mentioned above (Scheme S12 and Figure S15). Significantly, the starting dicationic expanded heterohelicene ExHHel1 was regenerated through the reverse reaction by reacting **ExHHel1-red** with a proton  $(H^+)$  source such as aqueous HNO<sub>3</sub> solution, via hydride-transfer to the proton (Figure 4A,F). This reversible hydride-generation and transfer phenomenon was found to be switchable for many cycles, as monitored by absorption spectroscopy (Figure 4G). Thus, the bis-imidazolium-based dicationic aza-anthracene core of the expanded heterohelicene molecule **ExHHel1** was proved to be an effective dynamic module to execute the stimuli-switchable reversible hydride storage/delivery chemistry, making the system a prospective chemical redox-switch in solution. Stimuliswitchable reversible hydride generation and transfer is of prime interest in several research fields including energy-storage/delivery,<sup>17</sup> CO<sub>2</sub> conversion,<sup>18</sup> biological redox processes<sup>19</sup> etc., and the here-discovered helicene molecules might be promising candidates toward such applications.

# Reversible Photochromic Behavior and Light-Controlled Photomechanical Spring-Like Motion

The photo-responsive dithienylethene (DTE)-type unit present in the expanded heterohelicene **ExHHel5**, in which the HOMO was located on the thiophene backbone, was next investigated as a non-invasive dynamic module toward potential photoswitch with photochromic readout. The yellow-colored solution of **ExHHel5** in acetonitrile showed a significant absorption band at 446 nm ( $\epsilon = 24020 \text{ mol}^{-1}\text{cm}^{-1}$ ). Irradiation of blue light (50 W) triggered cyclization reaction at the peripheral DTE sites (**ExHHel5** to **ExHHel5**'), suggested by a color change from yellow to green (Figure 5A,B). The cyclization process accompanied by an appearance of a new absorption band at 654 nm ( $\epsilon = 9860 \text{ mol}^{-1}\text{cm}^{-1}$ ) and an increase of the absorbance at 446 nm ( $\epsilon = 44400 \text{ mol}^{-1}\text{cm}^{-1}$ ) (Figure 5B). The appearance of the lower-energy absorption band at 654 nm indicates the formation of a more conjugated skeleton (in **ExHHel5'**) upon photoirradiation *via* an electrocyclic ring-closing reaction (Figure 5A).<sup>20</sup> The photoswitchable dynamic behaviour of this expanded heterohelicene was confirmed by achieving the reverse reaction, i.e., ring-opening from **ExHHel5'** to **ExHHel5**, using a higher wavelength light (red light, 50 W) (Figure 5C). The system showed excellent reversibility in acetonitrile solution (Figure 5D). Notably, the ring-closing response was quite fast, whereas prolonged ring-opening process suggests a relatively stable ring-closed isomer in photostationary state, similar to hindered diarylethenes.<sup>21</sup>

Interestingly, from computational studies, we found a reversible expansion and contraction behaviour at the helical rim of this photoswitchable expanded heterohelicene **ExHHel5**, upon light-induced ring-closing and ring-opening respectively (Figure 5E). This was plausibly associated with the reversible conformational (mechanical) distortion caused by the corresponding ring-closing and ring-opening stress at the peripheral sites, which eventually transmitted an opposite and reversible perturbation at the helical rim of the molecule. Thus, it was found that the helical pitch (centroid-centroid distance between two terminal overlapping rings A and I), changed by about 0.2 Å, along with the changes of about 4° and 12° in the intersecting angles between the terminal rings A or I, and the plane along the central pyridine ring E respectively, due to the photoswitching effect on **ExHHel5** (Figure 5E). This type of elastic elongation-contraction of the helical pitch essentially resembles a helical spring-like behaviour of the flexible  $\pi$ -expanded [13]helicene, investigated by Hirose and Matsuda via computational study.<sup>7b</sup> The authors also showed that the flexible helical molecules such as their [13]helicene, and [7]heliphene reported by Vollhardt,<sup>15</sup> possess small spring constant values (0.33, and 0.86 N·m<sup>-1</sup> respectively), suggesting the suitability of the molecules as soft molecular springs. In comparison, relatively rigid helicene, such as [7]helicene was found to have large spring constant value (3.07 N·m<sup>-1</sup>).<sup>7b</sup> Significantly, the present light-controllable helical spring-like behaviour in the designer molecule **ExHHel5** was featured with small spring constant value of



**Figure 5.** (A) Schematic representation of reversible photochromism of **ExHHel5**. (B) Absorption spectral profile of 30  $\mu$ M **ExHHel5** (in CH<sub>3</sub>CN) upon irradiation of blue light (50 W LED). Inset shows the increase of the absorbance value at  $\lambda_{max} = 654$  nm upon blue light irradiation. (C) Absorption spectral profile of 30  $\mu$ M **ExHHel5'** (in CH<sub>3</sub>CN) upon irradiation of red light (50 W LED). (D) Reversibility of photochromism of **ExHHel5** (10  $\mu$ M in CH<sub>3</sub>CN). The absorbance value at  $\lambda_{max} = 654$  nm was monitored for switching study upon consecutive irradiation of blue light for 3 min (green dots) and red light for 45 min (red dots). (E) Optimized structures and the geometrical parameters of the ring-open and ring-closed isomers of **ExHHel5** (Ph groups on the thiophene units were omitted for clarity) (6-31g(d,p)). (F) Plot of spring constant (*k*) values versus the inverse of third power of the helical dimeter (1/d<sub>h</sub><sup>3</sup>) for the expanded helicenes [13]helicene, **ExHHel5**, **ExHHel2** and [7]heliphene, along with a rigid helicene [7]helicene. (G) Schematic diagram of photochromism of **ExHHel5** in PMMA gel matrix coated on PET substrate. (G) Reversibility of photochromism of **ExHHel5** in PMMA gel matrix coated on PET substrate. The absorbance value at  $\lambda_{max} = 654$  nm was monitored for 3 min (green dots) and heating at 100 °C for 2 min (red dots).

0.76 N·m<sup>-1</sup>, indicating great flexibility of its helical rim (Figure S18c, SI). Moreover, the linear correlation of the spring constant (*k*) values to the inverse of third power of the helical dimeter  $(1/d_h^3)$ , for the photoswitchable **ExHHel5** molecule along with the other flexible congeners **ExHHel2**, [13]helicene, and [7]heliphene, and also the rigid [7]helicene molecule (Figure 5F), reflected the similarity in behaving like macroscopic springs which follow the relation  $k \propto d^{-3}$  (k = force constant, d = spring diameter).<sup>22</sup> Inspired by these analyses, and with a future aim to make the **ExHHel5** system suitable for practical applications, we tested its photoswitchable behaviour in the form of a PMMA (poly(methyl methacrylate)) polymer film matrix (2.3 wt%) on flexible PET (polyethylene terephthalate) substrate (Figure 5G). Delightedly, the system was found to be highly efficient and reversible in its operation in film as well (Figure 5H). Irradiation of blue light for 3 min led to a rapid color change of the film from yellow to green, as monitored by the change of absorbance at  $\lambda_{max} = 654$  nm. On the other hand, the reversion of the color from green to yellow was conveniently and rapidly performed by heating the film at 100 °C by exposing the film to hot air for just 2 min. Notably, the reverse reaction was also possible by irradiating red light, but the process was found to be slow in the thin film.

### Conclusions

In summary, we developed a convenient and simple synthetic protocol, termed as rollover  $\pi$ -expansion (RoPE), to access a novel class of flexible expanded heterohelicenes, with stimuli-responsive core and peripheral functional modules. Isolation and crystal structure analysis of the dirhoda-heterohelicene intermediate shed light on the origin of the expanded helicity in the final heterohelicene products, and supported by analyzing the crystal structures of two such products. The geometrical parameters of these molecules unambiguously suggested

expanded and flexible helicity within the helical rim. The photophysical and electrochemical properties were found to be highly tuneable based on the backbone and peripheral substituents of the molecules. The reversibly responsive dynamic behaviour was explored in two such helicene molecules using chemical redox and light as external stimuli, thus making them potentially effective toward reversible hydride storage/delivery system and light-controllable molecular spring-like system capable of reversible expansion/contraction at the helicene wings. The successful integration of the stimuli-controllable dynamic architectures within expanded heterohelicene backbone, as achieved in this work, would likely open up a door toward further sophisticated applications from the molecular and supramolecular engineering point of view.

### **Supporting Information**

Experimental details, computational details, and spectral details.

# **Conflict of Interest**

The authors declare no competing financial interests.

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