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Bistable Photoswitching of Hemithioindigo with Green and Red Light - Entry Point to Advanced Molecular Digital Information Processing

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Abstract

Photoswitches reacting to visible light instead of harmful UV irradiation are of very high interest due to the mild and broadly compatible conditions of their operation. Shifting the absorption into the red region of the electromagnetic spectrum usually comes at the cost of losing thermal stability of the metastable state - the switch switches off by itself. Only recently have photoswitches become available that combine visible light responsiveness with high bistability. However, shifting the wavelengths for bistable photoswitching beyond 600 nm is still a great challenge without involving secondary processes such as two-photon absorption or sensitization. We present a simple hemithioindigo photoswitch, that can efficiently be photoisomerized using green and red light while maintaining a high thermal barrier of the metastable state. This highly sought after properties allow for selective switching in a mixture of hemithioindigo dyes. In addition protonation can be used as second independent input altering the light response of the switch and allows construction of advanced molecular digital information processing devices. This is demonstrated by realizing a broad variety of logical operations covering combinational and sequential logic behavior. By making use of the protonation-induced loss of thermal bistability a high security keypad lock can be realized, which distinguishes the sequences of three different inputs and additionally erases its unlock state after a short time.

Introduction

Photoswitches are a class of molecules that undergo reversible changes upon irradiation with light. With this property they are key-components in a plethora of applications allowing to control events at the molecular scale with very high spatial and temporal resolution.[1] One key issue with many photoswitching systems is the wavelength of light that can be used to affect the molecular changes, especially if the geometry of the photoswitch has to be altered significantly by irradiation. For the most commonly used photoswitches - stilbenes, azobenzenes, diarylethenes, spiropyranes - at least one of the switching processes has to be triggered by damaging UV light, which limits applications in sensitive environments, especially in biology.[2] For reasons of penetration into tissues long wavelengths (close to 700 nm) are needed to produce maximum effects. To obtain photoswitches with strongly redshifted absorption the easiest approach is either increasing conjugation in the molecule or introducing donor-acceptor substituent pairs. However, such changes in the molecular structure typically result in a significant decrease of the thermal stability of the metastable isomeric state.[3] Although there are certain applications where thermally self-deactivating photoswitches are needed, the majority of applications demands bistable switches so that deactivation can be triggered in a controlled way by a second irradiation step. For these reasons great efforts have been made to shift the wavelengths of absorption of many classical photoswitches into the visible region while at the same time keeping a high thermal stability of the metastable state.[4] At the current state of the art only a very limited number of isomerization photoswitches are available that deliver such favorable combination of properties in a simple molecular setup[5] and without resorting to secondary processes like sensitization,[6] multiphoton absorption,[7] electron transfer,[8] upconversion,[9] or peptide conjugation[10] expedients. These simple photoisomerization systems achieve visible light induced and bistable switching in both directions mostly in the 400 nm to 560 nm region.[11] [12] [6b, 13] Examples that switch back and forth by direct visible light irradiation and at longer wavelengths >600 nm while keeping high thermal barriers between the individual states are known for diarylethenes[14] but are exceedingly rare when greater geometry changes such as double bond isomerizations are required.[5]

Interestingly there is another chromophore, which can be photoisomerized using visible light - even without any substitution at the core-dye structure - while displaying high thermal stability of the metastable state (i.e. a half life of 350 years at 25 °C). Despite these highly sought after properties hemithioindigo photoswitches[15] have been largely overlooked by the community and are scarcely applied so far - despite remarkably promising application examples.[16] In this communication we report on the photoswitching properties of a series of substituted hemithioindigo (HTI) photoswitches, which can be efficiently photoisomerized using visible light up to 625 nm while maintaining high thermal stability with a half life of the metastable *E* isomer of 30 days at 25 °C. This exceptional property profile is achieved in a simple molecular setup, which can easily be modified for further functionalization. In addition, protonation can be used as a second independent signal to shift the photoswitching wavelengths to the blue and at the same time decrease thermal bistability. The protonated form can also be photoisomerized in aqueous solution at low pH.

Results and Discussion

Redshifted Bistable HTIs HTI is a photoswitch that consists of a photoisomerizable C-C double bond, which connects a thioindigo fragment with a stilbene fragment (Figure 1). The absorption of unsubstituted HTI shows one maximum in the visible region of the spectrum for each, the thermodynamically stable *Z* (λ_{max} = 433 nm in CH_2Cl_2) and the metastable *E* isomer (λ_{max} = 457 nm in CH_2Cl_2), which is typically identified as the S_0 to S_1 transition. Substituents at the stilbene fragment only lead to a considerable redshift of absorption if they are in conjugation with the double bond and of strong donating character. Unfortunately this also leads to the typical decrease of thermal stability of the *E* isomer as can be seen for the already described HTIs **1** to **3**.[15b] In this work we have explored a different substitution position *para* to the sulfur atom of the thioindigo fragment. A series of derivatives **4** to **6** (Figure 1) was prepared with increasing donor strength of a substituent in the *para*-position to the sulfur atom and their photophysical properties were quantified with special emphasis on redshift of absorption and thermal stability of the metastable *E* isomer.

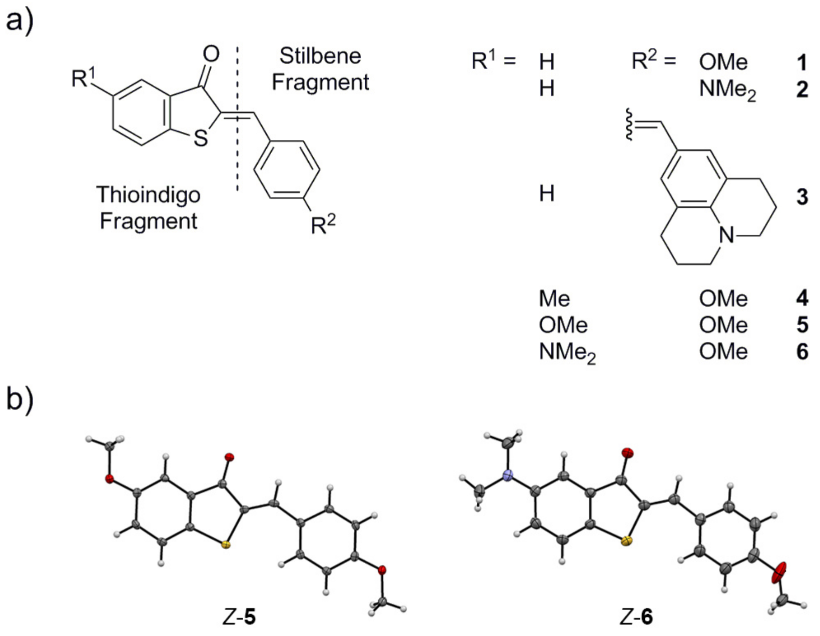
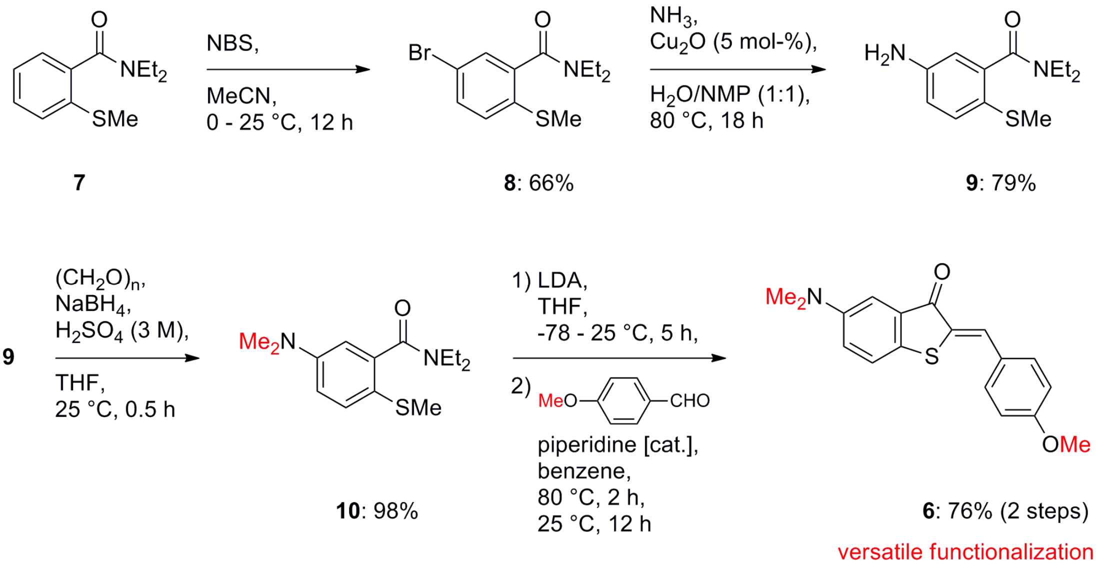


Figure 1 a) Substituted HTI photoswitches **1** to **6** investigated in this study. The two different molecular fragments are assigned. The thermodynamically stable *Z* isomers are shown. b) Crystal structures of HTIs *Z*-**5** and *Z*-**6**.

The synthesis of the most important derivative **6** is shown in Scheme 1, where it should be noted that this synthesis allows for easy introduction of functional groups on both, the thioindigo and the stilbene fragment in a convergent way. The synthesis starts from the known precursor *N*,*N*-diethyl-2-(methylthio)benzamide (**7**), which is selectively brominated in the *para*-position of the methylthio-substituent to give **8**. An Ullmann-type coupling introduces the amino group yielding aniline **9**, which subsequently can be alkylated using formaldehyde in a reductive amination reaction to yield **10**. At this point different functional groups can easily be introduced into the thioindigo fragment for further elaboration of the photoswitch. Deprotonation of the methylthio substitutent leads to formation of the intermediate benzothiophenone,[17] which is directly condensed with anisaldehyde to give **6**. By chosing different aldehydes, facile functionalization at the stilbene fragment can be realized.

Crystal structural analysis revealed complete planarity of *Z*-**5** and *Z*-**6** (Figure 1b), which leads to effective communication between the substituents on the thioindigo and stilbene fragments to the HTI core structure. Planarity of the structures is also observed in solution as a NMR-shift analysis reveals (see Supporting Information for more details).



Scheme 1 Synthesis of HTI **6** with strongly redshifted absorption. Both, the thioindigo and the stilbene fragment can easily be functionalized further (indicated in red).

HTIs *Z*-**1** to *Z*-**6** show distinctly different absorption maxima (Figure 2c) with a steady increase of the maximum wavelength of their S_0 to S_1 transition with increasing donor strength of their substituents (e.g. λ_{max} = 440 nm for *Z*-**1** to λ_{max} = ca. 500 nm for *Z*-**3** and *Z*-**6** in toluene). At the same time the extinction coefficients of this transition increase for *Z*-**1** to *Z*-**3** but decrease for *Z*-**4** to *Z*-**6**. The S_0 to S_2 extinctions show a steady decrease for *Z*-**1** to *Z*-**3** but no such regularity for *Z*-**4** to *Z*-**6**. The corresponding *E* isomers possess redshifted absorptions compared to the *Z* isomers and follow the same substituent trends in their extinctions. The observed regular absorption changes in **4** to **6** (Figure 2c) cannot easily be explained by a simple conjugation increase, as in the case of stilbene-substituted HTIs **1** to **3** (Figure 2a).[15b, 15c] Rather this behavior is another manifestation of Kauffmanns distribution rule of auxochromes, which was described for nitro-substituted resorcinols and related derivatives already in 1906.[18] The validity of this distribution rule for azobenezene derivatives was shown in 1911[19] and has found recent applications in the design of strongly redshifted photoswitches.[20] In our case the electronic interplay between the methylthio substituent and the electron-donor substituent at the thioindigo fragment (serving as the two auxochromic groups) is the cause for the increasingly redshifted absorptions.

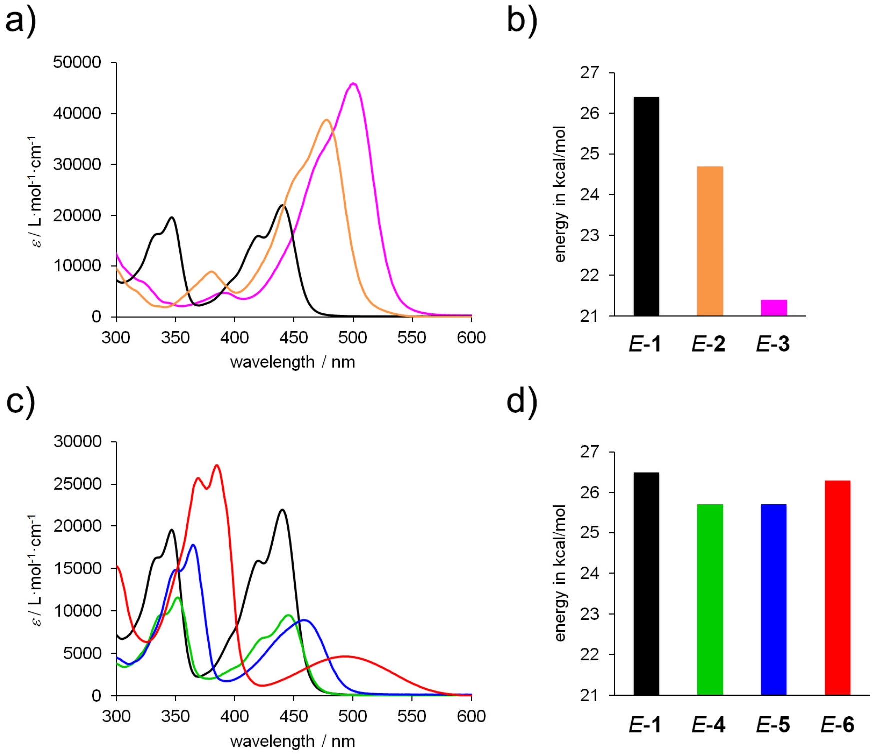


Figure 2 Extinction coefficients of the *Z* isomers and thermal stability of the *E* isomers of HTIs **1** to **6** in toluene solution. a) Extinction coefficients of HTIs *Z*-**1** to *Z*-**3**. b) Energy barriers of the thermal *E* to *Z* isomerization of HTIs *E*-**1** to *E*-**3**. c) Extinction coefficients of HTIs *Z*-**1** and *Z*-**4** to *Z*-**6**. d) Energy barriers of the thermal *E* to *Z* isomerization of HTIs *E*-**1** and *E*-**4** to *E*-**6**.

Because of their photochromism HTIs **1** to **6** photoisomerize efficiently and high yields of a single isomer can be obtained in the photostationary state (PSS) when using appropriate wavelengths for irradiation. The quantum yields of photoisomerization are found to be between 5 and 52% (the quantum yields for both switching directions are given in the supporting information for all HTIs **1** to **6**). The photoswitching properties of HTIs **1** to **3** have been thoroughly analyzed previously[15a, 15b, 15d, 15f] and served as the starting point for optimization. HTIs **1** to **3** bear substituents with increasing electron donor-capacity in the *para*-position of the stilbene fragment, which leads to a strong redshift of the absorption (e.g. λ_{max} = 500 nm for the julolidine derivative *Z*-**3** in toluene). Photoswitching can therefore be conducted with increasingly longer wavelengths (up to 625 nm for the *E* to *Z* photoisomerization of *E*-**3**) leading to high yields of the respective *Z* or *E* isomer.[15b] However, in this series a strong decrease of the thermal bistability is observed when increasing the substituent's donor strength, which significantly shortens the half life of the metastable *E* isomer down to 9 min at 25 °C for *E*-**3** (Figure 2b).

The introduction of electron donating substituents at the *para*-position of the sulfur atom in the thioindigo fragment allows circumventing this problem entirely, leading to photoswitches with vastly improved switching behavior. A methyl substituent in the *para*-position to the sulfur (HTI **4**[15e]) leads to no significant shift in the absorption spectrum compared to **1** but a notable decrease in extinction. Similar to HTI **1** very high isomer yields are obtained in the PSS when using blue (405 nm, >80% *E* isomer) and green (505 or 530 nm, >99% *Z* isomer) light for irradiation. The introduction of a methoxy substituent at the same position (HTI **5**) leads to a visible shift in the absorption profile with the maximum moving from 440 to 459 nm while the extinction again decreases. Also for HTI **5** high isomer yields in the PSS are obtained (71% *E* isomer with 420 nm, 98% *Z* isomer with 530 nm). Derivative **6** gives the most impressive performance with efficient *Z* to *E* photoisomerization at 470 nm (82% *E* isomer obtained in the PSS) and efficient *E* to *Z* photoisomerization at 625 nm (89% *Z* isomer obtained in the PSS). Instead of blue light, also green light at 505 nm can be used for the *Z* to *E* photoisomerization, which produces 80% of the *E* isomer in the PSS. Different solvents are applicable (toluene, THF, dioxane) without affecting the photoswitching properties (see Supporting Information). The thermal stability of the *E* isomers of HTIs **4** to **6** remains high throughout (25.7 to 26.5 kcal/mol i.e. half lifes of days to 1 month at 25 °C) and does not change significantly with substitution (Figure 2d). For *E*-**6** a barrier of 26.5 kcal/mol was obtained, which translates into a half life of 30 days at 25 °C. Thermal *E* to *Z* isomerization leads to quantitative formation of the *Z* isomers for all HTI derivatives. The miniscule influence of the substituents on the barrier of thermal *E* to *Z* isomerization for *E*-**4** to *E*-**6** can well be explained by their ineffective electronic communication with the isomerizing double bond. Therefore no stabilizing or destabilizing effects are transmitted from the substituent during thermal isomerization leading to a similar high barrier for all derivatives.

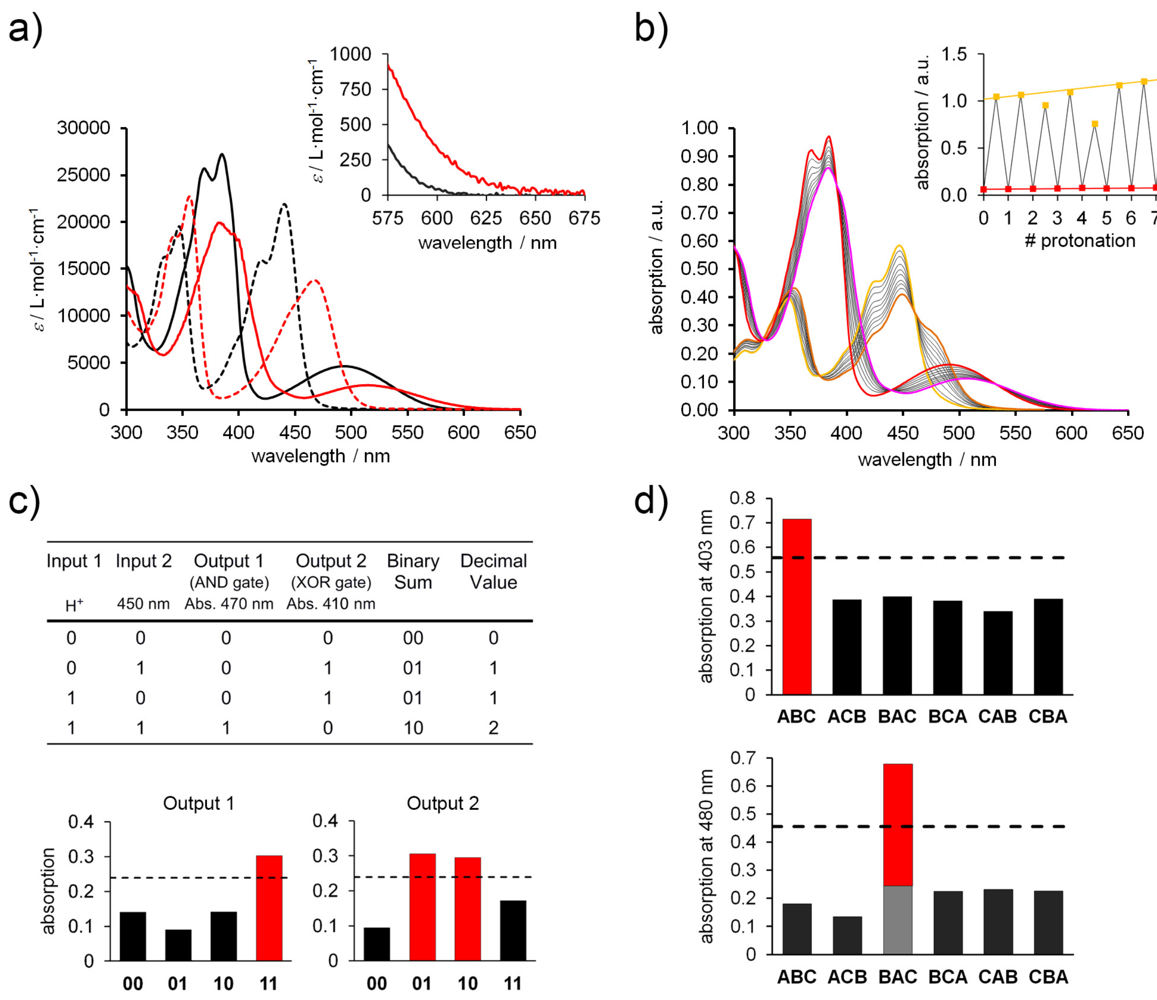
The different absorption profiles of HTIs **1** and **6** (Figure 3a) can effectively be used for wavelength selective photoswitching[16g, 21] and therefore allow to establish a number of distinguished bistable states in solution using four different wavelengths as input signals. Table 8S shows the composition of the different PSS. Although this combination does not constitute a fully orthogonal photoswitching system, highly selective and independent switching is possible without the need of changing the class of the photoswitch.[16g, 21b, 22]

Protonation Influences on HTI 6 and Molecular Digital Information Processing HTI **6** carries a basic amine substituent, which is the cause for the increased redshift of its absorption. The donating character of this substituent can be removed completely by simple protonation, which should result in dramatic changes of the photophysical properties. After addition of TFA to a THF solution of *Z*-**6** a strong hypsochromic shift of the absorption was observed with the maximum of the S_0 to S_1 transition moving to 450 nm (Figure 3b). The protonated HTI **6-H**$^+$ also undergoes efficient photoswitching with visible light (400 nm and 470 nm for the *Z* to *E* and *E* to *Z* photoisomerization, respectively) but shows a significantly decreased bistability (i.e. a barrier for the thermal *E* to *Z* isomerization of only 20 kcal/mol). Multiple protonation and deprotonation cycles can be performed without deterioration of the photoswitch in a biphasic mixture of $CHCl_3$ and H_2O using HCl and NaOH as acid and base, respectively. A biphasic mixture was used to leave the concentration of the photoswitch unaltered upon repeated acid and base additions. The protonated form **6**-H$^+$ can also be transferred to the aqueous phase (the final solution consisting of 1% TFA, 1% THF, and 98% H_2O) while retaining its switching capacity (see Figure 25S).

Since protonation significantly alters the absorption and irradiation response of HTI **6** it can be used as a second independent input signal leading to 2-bit digital information processing behavior.[23] To illustrate this we generated some of the most complex versions of such molecular devices, i.e. a Boolean half adder (Figure 3c) as example for combinatorial logic and a keypad lock[24] (Figure 3d) as example for sequential logic (with base addition as a third input). However, these are only two of many possible applications of HTI **6**, which is able to cover 14 of the 16 different possible output structures of a 2-bit system[25] and can also be used for reverse combinational logic processing (see the Supporting Information for more devices such as half substractor, digital comparator, 4:2 encoder, 2:4 encoder, or reversible XOR gate).

To configure a molecular Boolean half adder two input and two output signals are needed. We chose protonation and irradiation at 450 nm as respective Input 1 and Input 2 while the absolute absorptions at 470 nm and 410 nm are recorded as Output 1 (an AND gate) and Output 2 (a XOR gate), respectively. Output 1 and Output 2 are read out as being in the ON-state if they surpass a common threshold limit, which is illustrated in Figure 3c. Absorptions below this threshold are read as OFF-state. The truth table for the Boolean half adder is shown in Figure 3c, where Output 1 serves as the carry digit and Output 2 as the sum digit. The binary sum gives the final outcome of the addition process. If neither input is given the system stays in the initial *Z*-**6** form where both output signals remain below the threshold and are read out as OFF. The corresponding binary sum is therefore 0. If either Input 1 or Input 2 is given Output 2 is turned ON, as the absorbance at 410 nm is significantly increased for both *E*-**6** and *Z*-**6**-H$^+$. Absorbance at 470 nm remains below the threshold for these species keeping Output 1 in the OFF-state. Therefore either input alone leads to the binary sum of 1. Only if both inputs are given the species *E*-**6**-H$^+$ is formed, which absorbs strongly at 470 nm and thus surpasses the threshold of Output 2. At the same time *E*-**6**-H$^+$ possesses only a weak absorption at 410 nm turning Output 1 into the OFF state. The corresponding binary sum is therefore 2, which translates into an effective addition operation 1+1=2. Reset of the system is easily accomplished by a waiting time of 10 min (which can be shortened upon heating) and deprotonation by addition of triethylamine.

A first keypad lock can be realized by combining three input signals: protonation (Input A), deprotonation (Input B), and irradiation at 505 nm to the PSS (Input C); whereas recording the absorption of *E*-**6** at 403 nm serves as output signal. In order to guarantee similar conditions and no change of concentration during operation of the keypad lock a biphasic mixture of toluene and half saturated brine was used to alleviate the dilution effects of acid and base additions. The truth table for the keypad lock is shown in Figure 3d together with the different states of **6** generated by alternate sequences of the individual inputs. Starting from Z-**6**-H^+ only the sequence Input A, Input B, Input C produces *E*-**6** and generates a strong output signal. Note that the sequence Input C, Input A, and Input B could potentially also generate *E*-**6** but the finite time needed to add acid (Input A) after irradiation (Input C) leads to rapid thermal conversion of *E*-**6**-H^+ to *Z*-**6**-H^+ before the last input is given. Therefore, also this sequence produces *Z*-**6** as final result. All other sequences of the three inputs lead to formation of either *Z*-**6**-H^+, *Z*-**6**, or thermally unstable *E*-**6**-H^+ as final states, which do not absorb strongly at 403 nm (see experimental output entries Figure 3d top part). Consequently, only one correct sequence of the three different inputs unlocks absorption at 403 nm enabling sequential logic behavior of HTI **6** in solution. Reset of the system is conveniently done by a protonation step and 10 min waiting time. Another conceptually new keypad lock can be read out at the selective absorption of *E*-**6**-H^+ at 480 nm, which is only formed by the input sequence Input B (deprotonation), Input A (protonation), and Input C (irradiation with 420 nm) when starting from *Z*-**6**. Since *E*-**6**-H^+ is thermally unstable and quickly reverts to the thermodynamically more stable *Z*-**6**-H^+ this self-deactivation can be used to delete the unlock information after a short waiting time. In this way another level of “secrecy” can be introduced, allowing correct read out of the keypad lock only for a short time after the correct input sequence is given. Reset of the system is conveniently done by a protonation, 10 min waiting time, and deprotonation sequence.



Input 1 H^+	Input 2 450 nm	Output 1 (AND gate) Abs. 470 nm	Output 2 (XOR gate) Abs. 410 nm	Binary Sum	Decimal Value
0	0	0	0	00	0
0	1	0	1	01	1
1	0	0	1	01	1
1	1	1	0	10	2

Figure 3 Photoswitching of HTI **6**. a) The absorption profiles of HTIs **1** (dotted lines) and **6** (solid lines) in toluene solution are different enough to allow for light selective photoswitching. The extinction coefficients of the *Z* (black) and *E* isomers (red) are given. b) The photoswitching response of HTI **6** in THF solution (red to pink lines) can be shifted to shorter wavelengths by addition of TFA (yellow to orange lines). The inset shows multiple protonation and deprotonation cycles in a biphasic mixture of CH_3Cl and H_2O using HCl and NaOH as acid and base, respectively without changing the concentration of **6**. The absolute absorptions at 455 nm (yellow) and at 567 nm (red) are plotted. c) Truth table and experimental outputs for a Boolean half adder based on HTI **6**. Input 1 consists of protonation and Input 2 consists of irradiation with 450 nm light. Absorbance at 470 nm and 410 nm serve as Output 1 and Output 2, respectively. d) Experimental outputs for keypad locks based on HTI **6**. Input A consists of protonation, Input B of deprotonation, and Input C of irradiation with either 505 nm (top) or 420 nm (bottom) light. Absorbance of *E*-**6** at 403 nm (top) or of *E*-**6**-H^+ at 480 nm (bottom) serves as selective output for the keypad lock or a self erasing keypad lock, respectively. For the latter the output signals before (black and red bars) and after (grey bar) 5 min waiting time are shown.

Conclusions

In summary we have developed a simple HTI photoswitch **6**, which provides excellent bistable photoswitching using long wavelength irradiation. HTI **6** can be photoisomerized using green and red light up to 625 nm with high efficiency in a variety of solvents while displaying 30 day long half lifes of the metastable *E* isomer at 25 °C. Because of its redshifted absorption profile HTI **6** can be combined with HTI **1** in the same solution resulting in highly selective photoswitching between four distinguished states when using different wavelengths for irradiation. Protonation of this new chromophore constitutes a second independent input, which alters the irradiation response and allows construction of complex molecular digital information processing devices. Applications in combinational as well as sequential logic operations were demonstrated using HTI **6** as integrating system, but even more input-output structures can potentially be realized. In the future we will explore this new HTI for fully orthogonal photoswitching systems and elaborate information processing devices.[26] We would like to emphasize however, that the given application examples are just an illustration for the high potential of this new photoswitch. Due to the simple and easily functionalized molecular structure its redshifted absorption characteristics should be of great value especially for applications in the biological, medicinal, and supramolecular chemistry, as well as the material sciences.

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References

[1] a) M. M. Russew, S. Hecht, *Adv. Mater.* **2010**, *22*, 3348-3360; b) in *Molecular Switches*, Second ed. (Eds.: B. L. Feringa, W. R. Browne), Wiley-VCH Verlag GmbH & Co. KGaA, **2011**; c) in *Photochromic Materials*, First ed. (Eds.: H. Tian, J. Zhang), Wiley-VCH Verlag GmbH & Co. KGaA, **2016**, pp. 361-391; d) Z. Yu, S. Hecht, *Chem. Commun.* **2016**, *52*, 6639-6653; e) M. M. Lerch, M. J. Hansen, G. M. van Dam, W. Szymanski, B. L. Feringa, *Angew. Chem. Int. Ed.* **2016**, *55*, 10978-10999; f) J. Broichhagen, J. A. Frank, D. Trauner, *Acc. Chem. Res.* **2015**, *48*, 1947-1960; g) M. Qin, Y. Huang, F. Li, Y. Song, *J. Mater. Chem. C* **2015**, *3*, 9265-9275; h) H. K. Bisoyi, Q. Li, *Acc. Chem. Res.* **2014**, *47*, 3184-3195; i) R. Klajn, *Chem.*

Soc. Rev. **2014**, *43*, 148-184; j) W. Szymanski, J. M. Beierle, H. A. Kistemaker, W. A. Velema, B. L. Feringa, *Chem Rev* **2013**, *113*, 6114-6178.

[2] a) T. Goldau, K. Murayama, C. Brieke, S. Steinwand, P. Mondal, M. Biswas, I. Burghardt, J. Wachtveitl, H. Asanuma, A. Heckel, *Chem. Eur. J.* **2015**, *21*, 2845-2854; b) C. Brieke, A. Heckel, *Chem. Eur. J.* **2013**, *19*, 15726-15734; c) C. Brieke, F. Rohrbach, A. Gottschalk, G. Mayer, A. Heckel, *Angew. Chem. Int. Ed.* **2012**, *51*, 8446-8476; d) C. Beyer, H. A. Wagenknecht, *Synlett* **2010**, 1371-1376.

[3] Y. Yang, R. P. Hughes, I. Aprahamian, *J. Am. Chem. Soc.* **2014**, *136*, 13190-13193.

[4] a) D. Bleger, S. Hecht, *Angew. Chem. Int. Ed.* **2015**, *54*, 11338-11349; b) M. Dong, A. Babalhavaeji, S. Samanta, A. A. Beharry, G. A. Woolley, *Acc. Chem. Res.* **2015**, *48*, 2662-2670.

[5] M. Hammerich, C. Schutt, C. Stahler, P. Lentes, F. Rohricht, R. Hoppner, R. Herges, *J. Am. Chem. Soc.* **2016**.

[6] a) A. Cnossen, L. Hou, M. M. Pollard, P. V. Wesenhagen, W. R. Browne, B. L. Feringa, *J. Am. Chem. Soc.* **2012**, *134*, 17613-17619; b) V. W.-W. Yam, C.-C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 12734-12735; c) R. T. F. Jukes, C. Adamo, F. Hartl, P. Belser, L. De Cola, *Inorg. Chem.* **2004**, *43*, 2779-2792.

[7] a) J. Moreno, M. Gerecke, L. Grubert, S. A. Kovalenko, S. Hecht, *Angew. Chem., Int. Ed. Engl.* **2016**, *55*, 1544-1547; b) J. Croissant, M. Maynadier, A. Gallud, H. Peindy N'dongo, J. L. Nyalosaso, G. Derrien, C. Charnay, J. O. Durand, L. Raehm, F. Serein-Spirau, N. Cheminet, T. Jarrosson, O. Mongin, M. Blanchard-Desce, M. Gary-Bobo, M. Garcia, J. Lu, F. Tamanoi, D. Tarn, T. M. Guardado-Alvarez, J. I. Zink, *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 13813-13817; c) K. Mori, Y. Ishibashi, H. Matsuda, S. Ito, Y. Nagasawa, H. Nakagawa, K. Uchida, S. Yokojima, S. Nakamura, M. Irie, H. Miyasaka, *J. Am. Chem. Soc.* **2011**, *133*, 2621-2625.

[8] S. Lee, Y. You, K. Ohkubo, S. Fukuzumi, W. Nam, *Chem. Sci.* **2014**, *5*, 1463.

[9] a) J.-C. Boyer, C.-J. Carling, B. D. Gates, N. R. Branda, *J. Am. Chem. Soc.* **2010**, *132*, 15766-15772; b) L. Wang, H. Dong, Y. Li, C. Xue, L.-D. Sun, C.-H. Yan, Q. Li, *J. Am. Chem. Soc.* **2014**, *136*, 4480-4483.

[10] S. Samanta, A. A. Beharry, O. Sadovski, T. M. McCormick, A. Babalhavaeji, V. Tropepe, G. A. Woolley, *J. Am. Chem. Soc.* **2013**, *135*, 9777-9784.

[11] a) A. A. Beharry, O. Sadovski, G. A. Woolley, *J. Am. Chem. Soc.* **2011**, *133*, 19684-19687; b) R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Näther, F. Renth, F. Temps, *J. Am. Chem. Soc.* **2009**, *131*, 15594-15595.

[12] D. Bleger, J. Schwarz, A. M. Brouwer, S. Hecht, *J. Am. Chem. Soc.* **2012**, *134*, 20597-20600.

[13] a) T. Fukaminato, T. Hirose, T. Doi, M. Hazama, K. Matsuda, M. Irie, *J. Am. Chem. Soc.* **2014**, *136*, 17145-17154; b) M. J. Hansen, M. M. Lerch, W. Szymanski, B. L. Feringa, *Angew. Chem. Int. Ed.* **2016**, *128*, 16514-13518.

[14] a) G. M. Tsivgoulis, J. M. Lehn, *Adv Mater* **1997**, *9*, 627-630; b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685-1716.

[15] a) S. Wiedbrauk, H. Dube, *Tetrahedron Lett.* **2015**, *56*, 4266-4274; b) B. Maerz, S. Wiedbrauk, S. Oesterling, E. Samoylova, A. Nenov, P. Mayer, R. de Vivie-Riedle, W. Zinth, H. Dube, *Chem. Eur. J.* **2014**, *20*, 13984-13992; c) S. Wiedbrauk, B. Maerz, E. Samoylova, A. Reiner, F. Trommer, P. Mayer, W. Zinth, H. Dube, *J. Am. Chem. Soc.* **2016**, *138*, 12219-12227; d) A. Nenov, T. Cordes, T. T. Herzog, W. Zinth, R. de Vivie-Riedle, *J. Phys. Chem. A* **2010**, *114*, 13016-13030; e) T. Cordes, T. Schadendorf, B. Priewisch, K. Rück-Braun, W. Zinth, *J. Phys. Chem. A* **2008**, *112*, 581-588; f) T. Cordes, T. Schadendorf, K. Rück-Braun, W. Zinth, *Chem. Phys. Lett.* **2008**, *455*, 197-201; g) W. Steinle, K. Rück-Braun, *J. Org. Lett.* **2003**, *5*, 141-144.

[16] a) M. Guentner, M. Schildhauer, S. Thumser, P. Mayer, D. Stephenson, P. J. Mayer, H. Dube, *Nat. Commun.* **2015**, *6*, 8406; b) T. Lougheed, V. Borisenko, T. Hennig, K. Rück-Braun, G. A. Woolley, *Org. Biomol. Chem.* **2004**, *2*, 2798-2801; c) S. Herre, T. Schadendorf, I. Ivanov, C. Herrberger, W. Steinle, K. Rück-Braun, R. Preissner, H. Kuhn, *ChemBioChem* **2006**, *7*, 1089-1095; d) N. Regner, T. T. Herzog, K. Haiser, C. Hoppmann, M. Beyermann, J. Sauermann, M. Engelhard, T. Cordes, K. Rück-Braun, W. Zinth, *J. Phys. Chem. B* **2012**, *116*, 4181-4191; e) K. Eggers, T. M. Fyles, P. J. Montoya-Pelaez, *J. Org. Chem.* **2001**, *66*, 2966-2977; f) K. Tanaka, K. Taguchi, S. Iwata, T. Irie, *Supramol. Chem.* **2005**, *17*, 637-642; g) H. Dube, J. Rebek, Jr., *Angew. Chem. Int. Ed.* **2012**, *51*, 3207-3210; h) S. Kitzig, M. Thilemann, T. Cordes, K. Rück-Braun, *ChemPhysChem* **2016**, *17*, 1252-1263; i) M. Guentner, E. Uhl, P. Mayer, H. Dube, *Chem. Eur. J.* **2016**, *22*, 16433-16436.

[17] C. Mukherjee, A. De, *Synlett* **2002**, 325-327.

[18] H. Kauffmann, W. Franck, *Ber.* **1906**, *39*, 2722-2726.

[19] H. Kauffmann, W. Kugel, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2386-2389.

[20] M. Dong, A. Babalhavaeji, J. B. Hansen, L. Kalman, G. A. Woolley, *Chem. Commun.* **2015**, *51*, 12981-12984.

[21] a) D. Manna, T. Udayabhaskararao, H. Zhao, R. Klajn, *Angew. Chem. Int. Ed.* **2015**; b) H. Nishioka, X. Liang, T. Kato, H. Asanuma, *Angew. Chem. Int. Ed.* **2012**, *51*, 1165-1168; c) W.-C. Chen, Y.-W. Lee, C.-T. Chen, *Org. Lett.* **2010**, *12*, 1472-1475.

[22] M. M. Lerch, M. J. Hansen, W. A. Velema, W. Szymanski, B. L. Feringa, *Nat. Commun.* **2016**, *7*, 12054.

[23] a) K. Szaciłowski, *Chem. Rev.* **2008**, *108*, 3481-3548; b) D. Gust, J. Andreasson, U. Pischel, T. A. Moore, A. L. Moore, *Chem. Commun.* **2012**, *48*, 1947-1957; c) D. Gust, T. A. Moore, A.

L. Moore, *Chem. Commun.* **2006**, 1169-1178; d) A. P. De Silva, *Nature* **2008**, *454*, 417-418; e) A. P. De Silva, *Molecular logic-based computation*, PSC Publishing, **2013**; f) J. Andreasson, U. Pischel, *Chem. Soc. Rev.* **2010**, *39*, 174-188; g) S. Varghese, J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *Chem. Sci.* **2015**, *6*, 6050-6058; h) J. Andreasson, U. Pischel, *Chem. Soc. Rev.* **2015**, *44*, 1053-1069; i) S. Stockinger, O. Trapp, *Chem. Sci.* **2014**, *5*, 2677.

[24] a) D. Margulies, C. E. Felder, G. Melman, A. Shanzer, *J. Am. Chem. Soc.* **2007**, *129*, 347-354; b) Z. Guo, W. Zhu, L. Shen, H. Tian, *Angew. Chem. Int. Ed.* **2007**, *46*, 5549-5553; c) J. Lee, H. T. Chang, H. An, S. Ahn, J. Shim, J. M. Kim, *Nat. Commun.* **2013**, *4*, 2461.

[25] J. Andreasson, U. Pischel, S. D. Straight, T. A. Moore, A. L. Moore, D. Gust, *J. Am. Chem. Soc.* **2011**, *133*, 11641-11648.

[26] a) M. Balter, S. Li, J. R. Nilsson, J. Andreasson, U. Pischel, *J. Am. Chem. Soc.* **2013**, *135*, 10230-10233; b) P. Remon, M. Balter, S. Li, J. Andreasson, U. Pischel, *J. Am. Chem. Soc.* **2011**, *133*, 20742-20745; c) G. de Ruiter, M. E. van der Boom, *J. Mater. Chem.* **2011**, *21*, 17575; d) Q.-Q. Wu, X.-Y. Duan, Q.-H. Song, *The Journal of Physical Chemistry C* **2011**, *115*, 23970-23977; e) Y. Pan, Y. Shi, Z. Chen, J. Chen, M. Hou, C. W. Li, C. Yi, *ACS Appl. Mater. Interfaces* **2016**, *8*, 9472-9482; f) I. Gallardo, G. Guirado, J. Hernando, S. Morais, G. Prats, *Chem. Sci.* **2016**, *7*, 1819-1825; g) B. B. Cui, J. H. Tang, J. Yao, Y. W. Zhong, *Angew. Chem. Int. Ed.* **2015**, *54*, 9192-9197; h) A. Prasanna de Silva, *Chemistry - An Asian Journal* **2011**, *6*, 750-766; i) D. Ray, J. T. Foy, R. P. Hughes, I. Aprahamian, *Nat. Chem.* **2012**, *4*, 757-762.