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Donor-Acceptor Dihydropyrenes Switchable with Near-Infrared Light

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ABSTRACT: The use of low-intensity NIR light to operate molecular switches offers several potential advantages including enhanced penetration into bulk materials, in particular biological tissues, and reduced radiation damage due to the limited photon energies. The latter, however, pose a challenge for designing reasonably bistable systems. We have developed a general design strategy for direct one-photon NIR photoswitches based on negative photochromic dihydropyrenes carrying opposing strong donor–acceptor substituents either along the long axis of the molecule or across it. Thus, two series of 2,7- and 4,9-disubstituted dihydropyrenes were synthesized, and their photothermal properties



investigated as a function of the type, strength, and position of the attached donor and acceptor substituents as well as the polarity of the environment. By shifting the excitation wavelength deep into the NIR, both NIR one-photon absorption cross-section and photoisomerization efficiency could be maximized while retaining a reasonable thermal stability of the metastable cyclophanediene isomer. Thus, the lowest optical transition was shifted beyond 900 nm, the NIR cross-section was enhanced by two orders of magnitude, and the thermal half-lives vary between milliseconds and hours. These unique features open up ample opportunities for noninvasive, optically addressable materials and material systems.

■ INTRODUCTION

Photochromic molecules offer the great opportunity to change their intrinsic molecular properties (e.g., geometric and electronic structure, polarity, or charge distribution) dynamically and reversibly by applying light as an external stimulus.¹ The incorporation of such photochromic units in complex molecular systems enables a wide variety of applications in the fields of materials science,² devices,³ molecular machines,⁴ and life sciences.⁵ For most of these applications, visible or nearinfrared (NIR) light is more suitable than UV light due to its greater penetration depth and nondamaging character. Moreover, the use of NIR light to control a function of a complex system allows the presence of various other visible lightabsorbing functional molecules or chromophores without interfering with the photoisomerization process. However, the isomerization of molecular switches usually requires highenergy photons in at least one direction, which limits their utilization.

Photoswitches activated by red or NIR light have received increasing attention over the past decade, albeit impeded by the limited availability of photochemical transformations that require such low energies (<2.0 eV). This prompted the development of various red light activated photoswitches, such as protonated,⁷ coordinated,⁸ or bridged⁹ azobenzenes, indigoids,¹⁰ donor–acceptor Stenhouse adducts,¹¹ and binaphthyl-bridged imidazole dimers,¹² each with their own set of specific properties. However, it still remains challenging to

design a tunable photochromic system operable with real NIR light (>750 nm). Employing negative photochromic T-type photoswitches¹ opens up the opportunity to utilize visible or NIR light exclusively. Such systems benefit from the selective photoisomerization of the thermodynamically more stable state induced by low-energy light, in combination with a quantitative thermal reversion of the metastable isomer.¹³ Upon irradiation with light of longer wavelengths, an equilibrium is formed between the photochemical forward and thermal back reaction, which can be regulated by adjusting the light intensity, irradiation wavelength, or temperature or by modulating the thermal half-life to obtain the desired amount of photoproduct at the equilibrium state. Negative photochromism offers the additional advantage that the material composed of the stable form decolorizes as photoisomerization proceeds, resulting in increased optical transparency and thus further enhanced penetration depth. Nevertheless, it must be considered that there is an intrinsic connection between the required minimum excitation energy and hence maximum

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achievable bathochromic shift of the excitation wavelengths and the thermal stability of the metastable form.¹⁴ Therefore, the shift of the excitation wavelength deeper into the NIR region is inevitably tied to strongly diminished thermal halflives, which sets an upper limit.

Dihydropyrenes (DHPs) undergo a visible light-induced 6π cycloreversion to form decoupled and thus decolored cyclophanedienes (CPDs), which are metastable and thermally convert back to their fully aromatic form.¹⁵ Thus, this class of photochromic molecules fulfills the mentioned key criteria, rendering DHPs excellent candidates for the development of NIR photoswitches. Applying the general design principle of introducing "push-pull", i.e., donor-acceptor, substitution to the DHP scaffold allows to shift the absorption of the parent molecule from the visible to the NIR region. The donor and acceptor substituents are π -conjugated in the closed isomer, and hence the DHPs exhibit a partial quinoid character, giving rise to a long-wavelength transition, whereas in the open CPD isomer the donor and acceptor are cross-conjugated and thus decoupled, leading to a loss of the lowest energy transition (Figure 1).



Figure 1. Designing direct one-photon NIR photoswitches based on Don-Acc substituted DHPs: Closed isomers exhibit partial quinoid character with long-wavelength transitions allowing the conversion to thermally labile open isomers with far-red or NIR light.

Recently, we reported the first donor–acceptor DHP derivative, bearing simple dimethylamino and nitro substituents as a classic and strong donor–acceptor couple in the 4,9-positions, which allowed quantitative photoisomerization upon irradiation with NIR light.¹³ Here, we elucidate the effect of the substitution pattern, the donor–acceptor strength, and the polarity of the environment on the switching behavior and exploit this general design strategy to realize direct one-photon NIR photoswitches that can be operated up to 900 nm. We disclose the synthesis of various 2,7- and 4,9-donor–acceptor DHPs, analyze the efficiency of their NIR-induced ring-opening as well as the thermal half-life of their corresponding metastable CPDs, and present a theoretical explanation for the observed experimental results.

RESULTS AND DISCUSSION

Synthesis. Conjugation of the donor and acceptor groups in the closed DHP isomers is possible either in the 2,7positions, when introduced to the unsubstituted parent DHP 1, or in the 4,9-positions when starting from the 2,7bis(*tert*-butyl)DHP 2 (Scheme 1). The latter is synthetically more easily accessible (>8 g in 6 steps)¹⁶ as compared to 1 (ca. 3 g in 10 steps).¹⁷ In order to gain high synthetic flexibility to introduce a diverse set of donor and acceptor substituents, we first prepared both *pseudopara*-bromo-formyl precursors **3** and **4** via initial monobromination followed by a Rieche formylation. The bromo function provides a handle to introduce various donor substituents via palladium-catalyzed cross-coupling reactions, whereas the aldehyde function allows introducing acceptor substituents via a Knoevenagel condensation, which provides the additional benefit to elongate the π -system to gain an even larger red-shift of the absorption. In the synthesized two series of donor–acceptor DHPs, we introduced *N*-methylpyrrole and pyrrolidine as electron-donating groups, whereas malononitrile, indolenium, and tricyanofuran moieties were attached as electron-withdrawing groups (Scheme 1).

Comparing Substitution Patterns. UV-vis spectra of the synthesized donor-acceptor DHPs were recorded in degassed acetonitrile at 20 °C or -20 °C. All derivatives display a bathochromically shifted charge-transfer (CT) band in the far-red or NIR region of the spectrum ($\lambda > 750$ nm). The DHPs 2,7A and 4,9A bear N-methylpyrrole as a moderate donor and malononitrile as a strong acceptor substituent. Their red-shifted CT bands tail out up to $\lambda = 900$ and 800 nm, respectively, enabling both derivatives to be excited with NIR light (Figure 2). However, 2,7A, with the same donoracceptor substitution in the 2,7-position, displays the more pronounced batho- and hyperchromic effect on the lowest allowed transition, resulting in an NIR cross-section (definite integral of ε with $\lambda \ge 750$ nm) that is 31 times higher than the one of **4,9A**. In the latter, the *N*-methylpyrrole donor moiety is twisted out of the aromatic plane due to greater steric hindrance (dihedral angles are 29.8° for 2,7A vs 46.7° for 4,9A; for xyz-structures see the Supporting Information), thereby diminishing the influence of the donor-acceptor substitution.

Upon irradiation with either 780 or 730 nm LEDs, the intensity of the long-wavelength absorption bands of 2,7A and 4,9A, respectively, in acetonitrile decreases and an absorption feature in the UV region evolves (Figure 3, top). Since DHPs exhibit negative photochromism, the composition at the photothermal equilibrium¹⁸ (PTE) and the spectrum of the open isomer can directly be determined from the initial spectrum of the pure closed isomer and a corresponding irradiation spectrum (see Section 3.3 in the Supporting Information). The amount of open isomer at the PTE depends on the photoisomerization efficiency and the thermal half-life, which can effectively be influenced by modulating both light intensity and temperature. Under the applied conditions, 10% of 2,7A could be converted to the open isomer at -20 °C, while an almost quantitative conversion (>97%) could be achieved for 4,9A at 20 °C. In accordance with the abovementioned relation of the maximum bathochromic shift of the excitation wavelength and the thermal half-life of the metastable CPD isomer, 2,7A rapidly converts back to its closed form in the dark $(t_{1/2}(-20 \circ C) = 5 \text{ s})$, whereas the open isomer of 4,9A has a much higher thermal stability $(t_{1/2}(20 \text{ °C}) = 7 \text{ h})$ (Table 1; for further details see Section 3.4 in the Supporting Information).

Increasing Donor Strength. Replacing the moderately donating *N*-methylpyrrole with the stronger and sterically less demanding pyrrolidine donor significantly increases the partial quinoid character in DHP **2**,**7B** and **4**,**9B**, which in turn leads to an overall bathochromic shift of all optical transitions (Table 1).

Scheme 1. Synthetic Approach for Donor-Acceptor Functionalization of Dihydropyrenes^a



^{*a*}(a) NBS, 2,7: DMF, 0 °C, 94%, 4,9: DMF/DCM, -78 °C, 96%; (b) CHCl₂OCH₃, TiCl₄, DCM, 0 °C, 2,7: 60%, 4,9: 55%; (c) Don-H, Pd(OAc)₂, ligand, base, solvent, 90–100 °C, 2,7: 30–40%; (d) Acc-CH₂, pyridine, EtOH, reflux, 2,7: 50–85%, 4,9: 55–75% over two steps; (for details see Section 2 in the Supporting Information).



Figure 2. Absorption spectra of DHP 2,7A and 4,9A in acetonitrile at 20 °C including photographs of respective cuvettes (~20 μ M); gray area indicates NIR cross-section.

While the more pronounced quinoid character causes an immense increase of the intensity of the CT bands, the opposite can be observed for the absorption bands between 300 and 500 nm, which are associated with the aromatic DHP core itself (Figure 3, bottom). The photoisomerization of 2,7B could not be observed with steady-state absorption spectroscopy even at low temperatures down to -80 °C. This observation is reasonable considering that the activation barrier of the thermal ring-closure of the less red-shifted 2,7A is already very low ($\Delta G^{\dagger}_{o \to c}$ (20 °C) = 16.6 kcal mol⁻¹). It is important to note that although cooling to lower temperatures enhances the thermal half-life of the CPD isomer, it also decreases the efficiency of the photochemical DHP ring-opening due to a barrier, which has been predicted to be present in the excited state.²⁰ Nevertheless, DHP 4,9B, displaying a high NIR cross-section and a shift of the CT band

up to $\lambda = 900$ nm, still exhibits a thermal half-life of 2.7 min at 20 °C, which allows almost quantitative conversion (>94%) to the open isomer upon irradiation with an 810 nm LED (310 mW; see Figure S32 in the Supporting Information).

In principle, irradiation with increasing intensity shifts the equilibrium toward larger quantities of open CPD isomer in the PTE but may in addition cause reversible formation of endoperoxides (see Scheme S2 in Section 3.2 of the Supporting Information). DHPs are known photosensitizers able to generate singlet oxygen, which can subsequently react with the open isomer to form a CPD endoperoxide.²¹ Once small amounts of endoperoxide are formed, no clean isosbestic point and no first-order kinetics of the thermal reversion can be observed since both processes (photoisomerization and endoperoxide formation) are thermally reversible. However, endoperoxide byproduct formation could be overcome by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO),²² able to quench the generated singlet oxygen and thus ensuring clean conversion to the open isomer even during exposure to highintensity NIR light in the presence of oxygen (see Scheme S2 and Figure S35 in the Supporting Information).

Polarity of the Environment. The closed isomers of donor-acceptor DHPs display a pronounced positive solvatochromism due to a better stabilization of the zwitterionic resonance structure in more polar solvents, and thus the polarity of the environment has a tremendous effect on their photothermal properties. This solvent effect has been investigated for derivatives 2,7A and 4,9B in *n*-heptane, toluene, and acetonitrile. As expected, the molecular electrostatic potential of both derivatives shows a stronger charge separation in acetonitrile as compared to the nonpolar solvent *n*-heptane. Consequently, the partial quinoid character increases by altering the polarity of the solvent (Figure 4, top).

The effect is less pronounced for DHP 2,7A, which has the weaker donor-acceptor system. Nevertheless, already the



Figure 3. Top: Irradiation spectra (spectra taken every 12 s) in acetonitrile until reaching the PTE under the applied conditions; left: DHP **2,7A**: $-20 \degree C$, $17 \mu M$, 780 nm LED (fwhm = 30 nm, 330 mW); right: DHP **4,9A**: $20 \degree C$, $23 \mu M$, 730 nm LED (fwhm = 37 nm, 100 mW). Bottom: Comparison of absorption spectra in acetonitrile at 20 °C, gray area indicates NIR cross-section; left: DHPs **2,7A** and **2,7B**; right: DHPs **4,9A** and **4,9B**.

Table 1. Quinoid Character, Spectral Data, and Thermal Lifetimes of Open Isomers for 2,7A, 4,9A and 2,7B, 4,9B

		DHP			
		2,7A	4,9A	2,7B	4,9B
quinoid character ^a		7%	6%	16%	14%
$\lambda_{\text{onset}}^{b}$ [nm]		876	775	861	875
NIR cross-section	abs	7.7×10^{5}	2.5×10^4	4.9×10^{6}	1.6×10^{6}
	rel ^c	31	1	195	66
t _{1/2} (20 °C)		<540 ms ^d	7.1 h	n.a. ^e	2.7 min

^aBased on the harmonic oscillator model of aromaticity (HOMA;¹⁹ see Section 4.2 in the Supporting Information). ^b ε is 1% of ε at λ_{max} . ^cRelative to normalized NIR cross-section of **4**,**9A**. ^dExtrapolated to 20 °C (for further details see Section 3.4 in the Supporting Information). ^eNot available due to a short lifetime of the open isomer.

increase of the quinoid character from 5% to 7% is reflected in a bathochromic shift of the absorption onset of about 100 nm and an increased NIR cross-section. The enhanced thermal stability of the open isomer **2**,**7A** in the less polar solvents *n*-heptane and toluene ($t_{1/2}(20 \text{ °C}) = 7$ and 3 s, respectively) furthermore causes an increased extent of photoconversion (32% and 13%, respectively) upon irradiation with a 660 nm LED at 20 $^{\circ}$ C (Table 2; for further details see Section 3 in the Supporting Information).

The positive solvatochromism is more pronounced for derivative 4,9B, which has the stronger donor-acceptor system. The partial quinoid character almost doubles by altering the polarity of the solvent, which is reflected in a large bathochromic and hyperchromic effect on the CT band, leading to a shift of the absorption onset of around 70 nm and an increased NIR cross-section and is furthermore accompanied by a strong decrease of the thermal half-life from 4.4 h to 2.7 min (Table 2). In contrast to the closed form, the open isomers show no significant solvatochromism since the donor and acceptor are decoupled and no partial quinoid character is exhibited. The absorbance maximum of the open isomers of 2,7A and 4,9B is at $\lambda = 300$ nm in all investigated solvents, and the absorption tails out up to $\lambda = 600$ and 650 nm, respectively (Figure 4, bottom).

Calculated Thermal Relaxation and Activation Parameters. Solvent-dependent activation enthalpies of thermal ring-closure have been calculated for all investigated DHPs. However, activation entropies cannot be calculated accurately with an implicit solvation model since the structure of the solvation shell strongly affects the entropic contribution. Nevertheless, thermal reaction barriers of the recently reported 9-dimethylamino-4-nitro-DHP show a linear dependence on activation enthalpies and entropies,¹³ allowing the direct, linear



Figure 4. Top: Molecular electrostatic potential mapped on a 0.95 isosurface in *n*-heptane and acetonitrile. Bottom: Positive solvatochromism of DHP 2,7A (left) and 4,9B (right): Absorption spectra of closed (solid lines) and open isomers (dotted lines) in *n*-heptane, toluene, and acetonitrile at 20 $^{\circ}$ C.

		n-heptane	toluene	acetonitrile
			2,7A	
quinoid character ^a		4.7%	4.9%	7.2%
λ_{\max} [nm]		445 (18 920)	451 (18 750)	448 (18 710)
$(\varepsilon \ [L \ mol^{-1} \ cm^{-1}])$		652 (34 990)	668 (35 240)	671 (40 490)
$\lambda_{\text{onset}}^{b}$ [nm]		777	823	876
NIR cross-section	abs	4.8×10^{4}	3.3×10^{5}	7.7×10^{5}
	rel ^c	2	13	31
t _{1/2} (20 °C)		7 s	3 s	256 ms ^d
CPD present at PTE^{e}		32%	13%	n.a. ^f
			4,9B	
quinoid character ^a		8.0%	8.6%	14.2%
λ_{\max} [nm]		461 (28 480)	471 (25 750)	480 (18 940)
$(\varepsilon [L mol^{-1} cm^{-1}])$		706 (13 750)	724 (17 810)	780 (23 500)
$\lambda_{\text{onset}}^{b}$ [nm]		808	850	875
NIR cross-section	abs	1.4×10^{5}	5.8×10^{5}	1.6×10^{6}
	rel ^c	6	23	66
t _{1/2} (20 °C)		4.4 h	38 min	2.7 min
CPD present at PTE^{e}		98%	97%	94%

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^{*a*}Based on HOMA. ^{*b*} ε is 1% of ε at λ_{max} ^{*c*}Relative to normalized NIR cross-section of **4,9A** (see Table 1). ^{*d*}Extrapolated to 20 °C (see Section 3.4 in the Supporting Information). ^{*e*}Conversion under the applied conditions: 20 °C, **2,7A**: 660 nm LED (fwhm = 20 nm, 280 mW); **4,9B**: 810 nm LED (fwhm = 25 nm, 300 mW). ^{*f*}Not available due to a short lifetime of the open isomer.

correlation of measured thermal half-lives and calculated activation enthalpies. This relation can be employed to estimate the thermal half-life of the CPD isomer of derivative 2,7B at 20 °C to amount to just 14 ns (Table 3). Such a short thermal half-life cannot be measured by conventional steady-state UV–vis absorption spectroscopy, which is in accordance with our observation.

Table 3. Thern	nal Relaxation	and Activation	Parameters ⁴
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	DHP			
	2,7A	4,9A	2,7B	4,9B
$\Delta H^{\dagger}_{\mathrm{o} ightarrow \mathrm{c}}$ [kcal mol ⁻¹]	12.4	17.9	4.5	15.8
measured $t_{1/2}$ (20 °C)	256 ms ^b	7.1 h	n.a.	2.7 min
fitted $t_{1/2}$ (20 °C) ^c	359 ms	5.3 h	$14 \pm 6 \text{ ns}^d$	4.3 min
$\Delta H_{o \to c}$ [kcal mol ⁻¹]	21.5	16.3	28.4	16.7

^{*a*}Solvent: acetonitrile. ^{*b*}Extrapolated to 20 °C. ^{*c*}Fit function based on activation enthalpies, $R^2 = 0.9898$. ^{*d*}Uncertainty based on relative fit error (see Section 4 in the Supporting Information).

Interestingly, the thermal ring-opening activation enthalpies of all investigated DHPs are similar in the same solvent, independent of the attached donor–acceptor substituents, implying a comparable change of quinoid character from the closed isomer to the transition state in all cases. However, the absolute energies of the closed isomer and transition state strongly depend on the donor–acceptor system due to its π conjugation, whereas the energy of the open isomers is barely affected by the decoupled donor–acceptor system. Therefore, a linear relation between the thermal ring-opening activation and reaction enthalpy can be derived following the Bell–

Evans–Polanyi principle.²³ This relation allows a simple computational prescreening of the magnitude of thermal halflives of potential donor–acceptor DHPs based on fast optimizations of the open and closed minimum structures (see Section 4.6 in the Supporting Information). Moreover, the central carbon–carbon bond is the principal component of the reaction coordinate of the thermal ring-closure, effectively following Hammond's postulate.²⁴ The more exothermic the ring-closure is, the earlier the closed-shell singlet transition state and hence the lower the reaction barrier (see Section 4.6 in the Supporting Information). Two distinct linear trends occur for the 2,7- and 4,9-substitution pattern, displaying higher barriers for identical donor–acceptor groups in the latter case (Figure 5).



Figure 5. Activation enthalpies of the thermal ring-closure dependent on the central carbon–carbon distance. Precursor DHPs **6** and 7 bear formyl as a weak acceptor and *N*-methylpyrrole or pyrrolidine as donor groups, respectively, and were additionally calculated to prove the linear trend for the 2,7-substitution pattern.

Photoisomerization Efficiency. Since the measurement of quantum yields above 620 nm requires sophisticated techniques,²⁵ a more general and theoretical description of the photoisomerization efficiency has been chosen. However, we previously reported the ring-opening quantum yields for the less red-shifted 9-dimethylamino-4-nitro-DHP derivative at $\lambda = 579$ nm ($\Phi_{c \to o} = 0.28$ in *n*-heptane, 0.18 in toluene, and 0.05 in acetonitrile).¹³ Quantum chemical calculations may rationalize the increase of photochemical ring-opening efficiency in donor-acceptor DHPs both in nonpolar solvents and compared to the unsubstituted DHPs 1 and 2. Electron difference densities of the ground state and excited states calculated with ADC(2) show a charge-transfer character of the first excited state mainly caused by the HOMO-LUMO excitation contribution, whereas the second excited state corresponds mainly to an excitation of the DHP's aromatic core (Figure 6; see Table S6 in Section 4.4 of the Supporting Information). More importantly, a significant decrease of electron density along the central carbon-carbon bond takes place only during the first excitation, indicating that the photochemical ring-opening occurs from the first excited state. In contrast, the unsubstituted DHP undergoes the photoisomerization via the second excited state, explaining its low quantum yield for the ring-opening.^{18b} In nonpolar solvents, the decrease is more prominent, supporting the tendency of



Figure 6. Electron difference densities of the ground state and first and second excited state, respectively, of parent 2,7-bis(*tert*-butyl)-DHP 2, 4,9-NMe₂-NO₂-DHP (quinoid character: 5%), and 4,9B (quinoid character: 8%) in *n*-heptane.

higher quantum yields in less polar solvents (see Section 4.5 in the Supporting Information). In the series of the investigated donor-acceptor DHPs, the major contribution to the first excitation (HOMO-LUMO orbital substitution) remains almost constant, while the shape of the HOMO itself changes. The higher the solvent polarity, the more quinoid character the molecule adopts, and thus, donor and acceptor π -orbitals are in stronger conjugation with the aromatic system. An increased contribution of these π -orbitals leads to a decreased contribution of the central carbon-carbon bond region to the HOMO. Since the HOMO becomes depopulated during the first excitation, a weaker contribution of the carboncarbon bond to the HOMO implies a less pronounced decrease of electron density along the carbon-carbon bond but a stronger charge-transfer character. Thus, it turns out that the donor-acceptor substitution enhances the photochemical isomerization efficiency in the first place by enabling the ringopening from the first excited state. However, the photoisomerization efficiency decreases within the series of donoracceptor DHPs with an increase of quinoid character due to stronger charge-transfer and thus weaker carbon-carbon bond contribution to the first excitation (Figure 6; see Sections 4.1 and 4.5 in the Supporting Information).

Increasing Acceptor Strength and π **-System.** To find the lower limit for the excitation energy of donor-acceptor DHPs, we increased the acceptor strength and extended the conjugated π -system. Since the thermal stability of the open

attached an indolenium (C) or a tricyanofuran moiety (D) as stronger electron-withdrawing groups in combination with pyrrolidine as a strong donor exclusively in the 4,9-position. The selected strong acceptor groups additionally extend the conjugated π -system, resulting in red-shifted absorption spectra up to $\lambda = 966$ and 1017 nm of derivative 4,9C and 4,9D, respectively, and drastically increased extinction coefficients of the lowest transition (up to 85000 $L mol^{-1} cm^{-1}$) (see Figure S23 in Section 3.1 of the Supporting Information). Unfortunately, the photoisomerization of these derivatives could not be observed with steadystate absorption spectroscopy, although the thermal half-lives estimated by the calculated activation enthalpies are in the range of milliseconds to seconds, indicating genuinely low photoisomerization efficiencies. In addition, electron difference densities of 4,9C and 4,9D show no decrease of electron density along the central carbon-carbon bond in the first excited state, which illustrates the limits of utilizing even stronger donor-acceptor couples and more elongated π systems (see Sections 4.5 and 4.6 in the Supporting Information).

CONCLUSION

In conclusion, we have exploited the general design strategy for direct one-photon NIR photoswitches based on DHPs with strong donor-acceptor substituents attached in the pseudopara-positions, i.e., 2,7- and 4,9-disubstitution. Taking advantage of their negative T-type photochromism allows switching them entirely with far-red or NIR light. The developed synthetic route, starting from bromo-formyl DHP precursors, gives access to versatile donor-acceptor DHP derivatives. By merging experimental and theoretical approaches, we have been able to gain new insights into the underlying structure-property relationships and the photoisomerization mechanism of these derivatives, enabling us to tune their photothermal properties. The choice of the substitution pattern, the nature and strength of the donoracceptor system, and the polarity of the environment provide orthogonal handles for tuning the excitation wavelength, NIR cross-section, photoisomerization efficiency, and thermal halflife. Generally, the donor-acceptor substitution of DHPs enhances the quantum yield of the ring-opening proceeding via the first excited state. Although a tremendous increase of partial quinoid character in combination with an extended π -system gives rise to CT bands tailing beyond 1000 nm, the associated photoisomerization efficiency and thermal half-lives diminish and thus constitute an upper limit for the system. Nevertheless, we were able to shift the lowest allowed transition beyond 900 nm, increase the NIR cross-section by two orders of magnitude, and modulate the thermal half-lives between milliseconds and hours. These characteristics will be key to exploit such donor-acceptor DHPs for various applications ranging from photoactive materials² and optoelectronic devices³ all the way to optobiology.⁵

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c04219.

Optimized structures in XYZ file format (ZIP)

Experimental procedures, characterization data, spectroscopic data, and computational data (PDF)

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Notes

The authors declare no competing financial interest.

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