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Design, synthesis and photoisomerization behavior of novel azobenzene-based dyes

containing different alkyl chains and isolation groups

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Abstract

A series of reactive azo dyes based on 4-phenylazophenol, containing hexenyloxy-, allyloxyethoxy-propoxy- and tetramethyl-disiloxanyl-propoxy substituents were synthesised. Additionally, allyl-functionalized azo-based chromophores with changeable isolation groups (hydroxymethylene-, trimethylsiloxymethylene- and pentafluorophenoxymethylene-) as well as with an additional azobenzene unit were successfully obtained. The photoisomerization behaviors of the synthesized azo dyes were investigated in solution as well as in films. Importantly, the occurrence of photoisomerization (at least near the surface after UV treatment) was confirmed in the crystalline dye films. The resulting compounds can be employed for the synthesis of a wide variety of azo-based materials which may be suitable for optical and electrooptical applications.

Keywords: azo dyes, photoisomerization, isolation group, chromophore-chromophore aggregation

Introduction

Organic dyes containing an azobenzene fragment are extensively used as tunable and lightresponsive chromophores due to reversible *cis-trans* photoisomerization.¹⁻¹⁰ This isomerization is reversible by photochemical and thermal pathways. However, the low thermal stability of azobenzene dyes and high ability to aggregate in the solid phase have limited their applications in devices.¹¹⁻¹⁴ One approach to solve these problems is to incorporate the organic azo chromophores into a polymer backbone (generally, polymers with azo units in the side chains) as well as the polyhedral oligomeric silsesquioxane (POSS) core.¹³⁻²⁰ Additionally, such azo-containing systems are able to form uniform and ultrathin films. It is known that organic films which are smooth and homogeneous over large areas possess advanced optic and optoelectronic properties.²¹ Many potential applications have been proposed for azo-containing polymers or star-shaped molecules with the POSS core and azobenzene dye arms, such as optical data storage, liquid crystal displays, molecular switches, nonlinear optical devices, surface relief gratings, and as a stable active medium to induce reversible plasmonic modulations of embedded metal nanostructures. Therefore, the development of new azo-containing dyes bearing reactive substituents is of significant importance.

Literature reports have clearly demonstrated that the flexible spacer chain length of azobenzene dyes plays an important role in regulation of the optical and liquid crystalline properties of materials based on such dyes.^{17, 20, 22-26} Thus, it is crucial to control the distance between the azobenzene unit and the terminal reactive group, that is, to regulate the spacer chain length of dyes. At the same time the influence of the chemical nature of flexible alkyl chains on the photoisomerization behavior of azo-containing materials has been poorly studied. On the other hand, incorporation of bulky groups into the azo chromophore with constant spacer lengths between the azo dyes and medium (polymer, POSS) represents another effective way to regulate the photooptical properties of azo-containing materials. More importantly, these chemical bulky groups can suppress crystallization of azo-containing materials (crystallinity leads to poor quality film surfaces) as well as serve as so-called suitable

isolation groups which are introduced to decrease the intermolecular dipole-dipole interaction of chromophore fragments.²⁷⁻²⁹

Thus, the current work represents an approach to the design of reactive azobenzene dyes possessing flexible alkyl chains of different chemical natures and lengths as well as azo dyes containing allyl tails and isolation groups of different sizes. Additionally, the photoisomerization behavior of the synthesized dyes were thoroughly investigated in solution as well as in films.

Results and discussions

For the synthesis of dyes **3**, **5** and **7** containing flexible and reactive hexenyloxy-, allyloxyethoxy-propoxy-, and tetramethyl-disiloxanyl-propoxy fragments, respectively, commercially available 4-phenylazophenol (**1**) was chosen as the initial precursor (Scheme 1). The obtained dye **2**, synthesised according to a literature method,²² was readily transformed into the corresponding hexenyloxy-substituted dye **3** by dehydrohalogenation using the KOH-ethanol system. It should be noted that the synthesis of azo dye **3** has previously been reported from dye **1** and the prohibitively expensive 6-bromo-1-hexene.²⁰ However, our approach to the synthesis of dye **2** provides an easy and inexpensive synthetic method. Dye **5** with the allyloxy-ethoxy-propoxy substituent was prepared *via* etherification of compound **1** with excess 1,3-dibromopropane,³¹ and subsequent reaction of dye **4** with 2-allyloxyethanol in the presence of NaH.

Several recent studies demonstrated that inserting a flexible disiloxane segment into the lateral alkyl chain of azo dyes can improve their photo-responsive properties.^{32,33} Therefore, 1,1,3,3-tetramethyldisiloxane was used for the synthesis of dye **7** containing the tetramethyl-disiloxanyl-propoxy substituent, and consequently, the terminal hydride functional group. Thus, dye **6** was synthesized from the reaction of dye **1** with allyl bromide¹⁹ and subsequently converted into the azo chromophore **7** *via* a hydrosilylation reaction. A 8-fold excess of 1,1,3,3-tetramethyldisiloxane was used to ensure formation of the mono-substitution product.



Scheme 1. Synthetic pathways for the synthesis of dyes 3, 5 and 7.

Hence, the synthesized dyes **3**, **5** and **7** consist of the following structural units: azobenzene fragments, flexible spacers of different lengths and a terminal reactive vinyl group (**3** and **5**) or Si-H group (**7**).

The introduction of isolation groups to the chromophore moieties should be an efficient approach to minimize azobenzene aggregation and the crystallinity of materials based on such dyes. Thus, we chose 5-[2-phenyldiazen-1-yl]-2-(prop-2-en-1-yloxy)benzaldehyde (8),³⁴ carrying the reactive aldehyde group at the *ortho*-position to the allyloxy-fragment of the aromatic ring, as a scaffold for the attachment of a variety of isolation groups, including an additional azobenzene unit (Scheme 2).



Scheme 2. Synthesis of dyes 9-12.

The synthesis of azo dye 9 containing a hydroxymethylene group on the aromatic ring was accomplished by reduction of the aldehyde group of dye 8 with NaBH₄. The obtained dye 9, due to the presence of the vinyl group, can be potentially used for hydrosilylation reactions with Si-H containing compounds. In that context, protection of the hydroxyl groups of dye 9 is essential because they can easily react with Si-H bonds (O-silylation).^{35,36} Thus, we obtained the trimethylsilyl-protected dye 10 (Scheme 2), and hence, OH-functionalized materials can be easily prepared where necessary. Notably, dye 10 was easily hydrolyzed by atmospheric moisture. As a result, the photoisomerization behavior of dye 10 was not studied. Although dye 10 is easily hydrolyzed, it may provide a useful starting material for subsequent reactions, and due to the presence of the hydroxyl group, it is capable of further functionalization.

It is known that perfluoroaromatic rings are electropositive, which could lead to reversible selfassembly between the non-fluorinated aromatic units and the perfluoroaromatic units $(Ar-Ar^F$ interactions).^{37,38} Thus, we obtained the pentafluorophenyl-bearing dye **11** by the reaction of dye **9** with excess hexafluorobenzene (Scheme 2).

Furthermore, a new azo-chromophore **12** was synthesized *via* etherification of compound **8** with dye **2**. The additional azobenzene unit could act as an isolation group, and eventually to prevent crystallization of the azo-containing materials based on dye **12**. Additionally, the synthesis of dyes with two azobenzene groups is an approach to increase chromophore concentration. Due to the presence of reactive functional groups, the resulting vinyl-containing azo dyes (**3**, **5**, **9**, **11** and **12**) and dye **7** with the tetramethyl-disiloxanyl-propoxy fragment can be attached to the structure of hydride (e.g. octakis-(dimethylsilyloxy)silsesquioxane) or vinyl-containing (e.g. octavinyl polyhedral oligomeric silsesquioxane) medium *via* hydrosilylation reactions.

All of the synthesized dyes belong to the azobenzene type molecules according to Rau classification.^{39,40} The structures of the synthesized compounds were determined by IR, UV-Vis, ¹H, ¹³C, ¹⁹F NMR, and mass spectrometry techniques, and were in full agreement with the proposed structures (ESI, Fig. S1-S8). The electronic absorption spectra of the prepared dyes exhibit two characteristic absorption bands. The high intensity band at 343–347 nm is related to π - π * transition of the *trans* form of the azobenzene moiety. The weak band in the range of 427–443 nm originates from typical n- π * transition.

The alkyl tail lengths of azo compounds **3** (0.86 nm), **5** (1.31 nm) and **7** (0.92) were calculated using quantum-chemical calculations (ESI, Fig. S9). Although the alkyl chain lengths of azo dye **3** and **7** were comparable, they have different chemical structures.

Figure 1 represents the electronic absorption spectra of dyes 5, 11 and 12 and the kinetics of the *cis-trans* photoisomerization of dyes 3, 5, 7, 9, 11 and 12 in CHCl₃. The photoisomerization spectra of dyes 3, 7 and 9 are reported in the ESI (Fig. S10). It was found that photoisomerization reached a photostationary state within 35 s for solutions of dyes 3, 5 and 7, within 50 s for solutions of dyes 9 and 11, and within 40 s for solutions of dye 12. As seen in Figure 1 the intensity of the absorption band at 343-347 nm (π - π * transition) decreased progressively, while the absorption band corresponding to the n- π * transition in the *cis* isomer at 427–443 nm increased with irradiation time, suggesting that

isomerization of the azobenzene chromophore from the *trans* to *cis* form occurs until a photostationary state is reached.



Figure 1. UV-vis spectra of dyes (a) 5, (b) 11 and (c) 12 under UV irradiation at 365 nm.
(d) Kinetics of the *cis-trans* isomerization of dyes 3 (line a), 5 (line b), 7 (line c), 9 (line d), 11 (line e) and 12 (line f) in CHCl₃ solution.

Compounds **3**, **5** and **7** had similar observed photoisomerization rate constants: 0.131 ± 0.031 s⁻¹, 0.118 ± 0.027 s⁻¹ and 0.126 ± 0.026 s⁻¹, respectively, which indicate that the length of aliphatic fragments has no significant effect on the photoisomerization. The photoisomerization rates of dyes **9** and **11** with lateral substituents in the *ortho* position to the ether linkage of the azobenzene fragment were

relatively slower compared to dyes **3**, **5** and **7**. Evidently, the reduced rate of photoisomerization may be attributed to the change of the electronic nature of the azobenzene fragment. The values of photoisomerization rate constants were 0.055 ± 0.013 s⁻¹ for dye **9** and 0.058 ± 0.013 s⁻¹ for dye **11**. The chemical structure of azo dye **12** can be defined as a hybrid structure of the two dye types: (i) dyes without the isolation group (**3**, **5** and **7**) and (ii) dyes with isolation groups (**9** and **11**). Evidently, the photoisomerization rate of the azobenzene unit without the lateral substituent of dye **12** is faster compared to the azobenzene unit with lateral substituents in the *ortho* position to the ether linkage. For this reason, the rate constant of dye **12** was 0.096 ± 0.021 s⁻¹ which was higher than those for dyes **9** and **11**, but lower than dyes **3**, **5** and **7**. It should be noted that all obtained azo dyes have shown a similar reverse isomerization ability induced by irradiation with visible light (ESI, Fig. S11).

Next, we investigated the formation of films from the azo dyes by multi-step drop-casting toluene solution onto glass substrates treated with poly(1-vinylpyrrolidone-co-styrene). All azo dyes gave discontinuous and inhomogeneous films due to crystallization and aggregation. Thus, transmission and reflection optical microscopy (TOM and ROM, respectively) revealed the crystalline structure of azo dye **3**, **9** and **11** (ESI, Fig. S12). A very rough film surface was observed for hybrid azo dye **12**. In general, it appears that the longer alkyl tails of azobenzenes **5** and especially **7** have a positive effect on film-forming properties. Although azo-dye molecules **5**, **7** and **12** are arranged in an ensemble of clumps of different sizes in their films, these dyes gave somewhat more uniform and amorphous films with a decreased microroughness. Evidently, the covalent linkage of the obtained dyes to the polymer backbone or POSS molecules will facilitate the formation of uniform ultrathin films.

UV-vis absorption spectra are sensitive to the interchromophore distance and orientation, and UV-vis spectroscopy is a useful tool to evaluate the aggregation effect of organic dyes.⁴¹ The absorption band corresponding to π - π * transition in the *trans* isomer of all dye films (especially for crystalline films of azo dyes **3**, **9** and **11**) was broad (Fig. 2 and ESI, Fig. S13). This may be due to the partial chromophore-chromophore aggregation of the azo dyes. Thus, the H- and J-aggregation of

azobenzene normally will result in the blue and red shift of maximum absorption band.⁴² The absorption band (π - π * transition) of dye 7 is only slightly broader compared to its solution absorption (Fig. 2a and ESI). Apparently, this is associated with the optimal quality of azo dye 7 film.



Figure 2. (a) Photoisomerization of dye **7** in film. (b, c) UV-vis spectra of (b) dye **9** and (c) dye **11** films after irradiation with UV light (365 nm). (d) Photoisomerization of dye **11** in film after UV light annealing at 365 nm.

Importantly, the *trans-cis* photoisomerization of azobenzene still occurs in films based on dyes **5** and **7**, containing flexible allyloxy-ethoxy-propoxy- and tetramethyl-disiloxanyl-propoxy fragments respectively, as well as "hybrid" dye **12**. It is worth noting that the photoisomerization of these dyes in films was much slower than in solution. For example, a photostationary state for dye **5** was observed

after 20 min UV irradiation. At the same time it was observed that the photoisomerization rate and the isomerization degree at the photostationary state significantly depend on the film thickness. Thus, the photoisomerization rate constants of the investigated azo dye films were not calculated since the drop-coated films from each dye were too varied in thickness for reliable measurement.

Interestingly, when solid films of azo dyes **3**, **9** and **11** were UV irradiated up to 12 min, the maximum of $n-\pi^*$ electronic transitions of azobenzene chromophores (~440 nm) continuously increased and the maximum of π - π^* electronic transitions also increased (gradually) (Fig. 2b, c and ESI, Fig. S13). Clearly, the intensity of the maximum *cis* absorption band increases as a result of *trans*-to-*cis* photoisomerization. The formation of *cis* azobenzene isomers results in the destruction of the face-to-face interactions of planar the *trans*-azobenzene moieties that lead to the increase of intensity of the *trans* band. Further UV irradiation, up to 35 min, resulted in a further increase of absorption intensity of the *trans* band and absorption suppression at ~440 nm (*cis* absorption). Further UV irradiation of the azo dye **11** film to 85 min led to a decrease of both the maximum of π - π^* and n- π^* electronic transitions (Fig. 2c). The most likely interpretation for this is that recrystallization occurred with the formation of more stable *trans*-azobenzene structures and subsequent generation of their aggregates.

In general, UV annealing can significantly improve the different properties of the films and promote recrystallization so as to form preferred structures.⁴³ Thus, the photoisomerization behavior of dye **11** film after irradiation with UV light (365 nm, 1 h) and white light (>450 nm, 5 min) at room temperature was examined. As seen from Figure 2d, surprisingly, the annealed sample film showed typical photoisomerization behavior of the azobenzene moieties upon UV excitation and reaches a photostationary state after about 10 min. Normally, *trans-cis* photoisomerization of azobenzene chromophores is not observed in the bulk crystalline state because of the large geometric changes that would be required in such densely packed crystal lattices.⁴⁴ However, it was shown that photoisomerization near the surface of crystals can occur.⁴⁴ This aspect of the photoisomerization behavior will be investigated in greater detail in due course.

In summary, a series of reactive azo dyes based on 4-phenylazophenol and containing hexenyloxy-, allyloxy-ethoxy-propoxy- and tetramethyl-disiloxanyl-propoxy substituents were synthesized. Additionally, we developed synthetic routes for several new azo-based chromophores with changeable isolation groups (hydroxymethylene-, trimethylsiloxymethylene-, pentafluorophenoxymethylene- and azobenzene groups) as well as with an allyl tail. Typical photoisomerization behavior was observed for all synthesized dyes in solution. The results of photoisomerization experiments in solution show that introduction of side isolation substituents in the ortho-position to the ether linkage of the azobenzene fragment of the dyes results in a decrease of photoisomerization rate constants. More importantly, the occurrence of photoisomerization (at least near the surface of crystalline films) was confirmed in the solid state of the azo dyes films. It is reasonable to suggest that the obtained dyes can be considered for the synthesis of different azocontaining materials based on POSS compounds or polymers and have good prospects for usage as nanometer sized photoswitches, active layer materials with optical-limiting properties, and a medium with photoinduced anisotropy for optical storage.

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References and notes

- 1. Dugave, C.; Demange, L. Chem. Rev. 2003, 103, 2475.
- 2. Bandara, H.M.D.; Burdette, S.C. Chem. Soc. Rev. 2012, 41, 1809.
- Vapaavuori. J.; Goulet-Hanssens, A.; Heikkinen, I.T.; Barrett, C.J.; Priimagi, A. Chem. Mat. 2014, 26, 5089.
- Schultz, T.; Quenneville, J.; Levine, B.; Toniolo, A.; Martínez, T.J.; Lochbrunner, S.; Schmitt, M.; Shaffer, J.P.; Zgierski, M.Z. Stolow, A. J. Am. Chem. Soc. 2003, 125, 8098.

- Biradar, S.; Kasugai, R.; Kanoh, H.; Nagao, H.; Kubota, Y.; Funabiki, K.; Shiro, M.; Matsui, M. Dyes Pigm. 2016, 125, 249.
- Miniewicz, A.; Tomkowicz, M.; Karpinski, P.; Sznitko, L.; Mossety-Leszczak, B.; Dutkiewicz, M. Chem. Phys. 2015, 456, 65.
- 7. Dai, S.; Ravi, P.; Tam, K.C. Soft Matter 2009, 5, 2513.
- Shevchenko, V.V.; Sidorenko, A.V.; Bliznyuk, V.N.; Tkachenko, I.M.; Shekera, O.V. Polym. Sci. Ser. A+ 2013, 55, 1.
- Guo, S.; Matsukawa, K.; Miyata, T.; Okubo, T.; Kuroda, K.; Shimojima, A. J. Am. Chem. Soc. 2015, 137, 15434.
- Adachi, H.; Hirai, Y.; Ikeda, T.; Maeda, M.; Hori, R.; Kutsumizu, S.; Haino, T. Org. Lett. 2016, 18, 924.
- 11. Chen, T.; Xu, S.; Zhang, F.; Evans, D.G.; Duan, X. Chem. Eng. Sci. 2009, 64, 4350.
- 12. Wu, W.; Ye, C.; Qin, J.; Li, Z. Polymer 2012, 53,153.
- 13. Chi, H.; Mya, K.Y.; Lin, T.; He, C.; Wang, F.; Chin, W.S. New J. Chem. 2013, 37, 735.
- 14. Zhou, J.; Zhao, Y.; Yu, K.; Zhou, X.; Xie, X. New J. Chem. 2011, 35, 2781.
- 15. Wang, D.; Wang, X. Prog. Polym. Sci. 2013, 38, 271.
- 16. Fernández, R.; Etxeberria, H.; Eceiza, A.; Tercjak, A. Eur. Polym. J. 2013, 49, 984.
- Miniewicz, A.; Girones, J.; Karpinski, P.; Mossety-Leszczak, B.; Galina, H.; Dutkiewicz, M. J. Mat. Chem. C. 2014, 2, 432.
- 18. Su, X.; Xu, H.; Deng, Y.; Li, J.; Zhang, W.; Wang, P. Mat. Lett. 2008, 62, 3818.
- Ledin, P.A.; Tkachenko, I.M.; Xu, W.; Choi, I.; Shevchenko, V.V.; Tsukruk, V.V. *Langmuir* 2014, 30, 8856.
- 20. Ledin, P.A.; Russell, M.; Geldmeier, J.A.; Tkachenko, I.M.; Mahmoud, M.A.; Shevchenko, V.; El-Sayed, M.A.; Tsukruk V.V. ACS Appl. Mat. Interfaces 2015, 7, 4902.
- Tenent, R.C.; Barnes, T.M.; Bergeson, J.D.; Ferguson, A.J.; To, B.; Gedvilas, L.M.; Heben, M.J.;
 Blackburn, J.L. Adv. Mater. 2009, 21, 3210.

- 22. Zhang, X.A.; Zhao, H.; Gao, Y.; Tong, J.; Shan, L.; Chen, Y.; Zhang, S.; Qin, A.; Sun, J.Z.; Tang, B.Z. *Polymer* 2011, *52*, 5290.
- 23. Li, X.; Fang, L.; Hou, L.; Zhu, L.; Zhang, Y.; Zhang, B.; Zhang, H. Soft Matter 2012, 8, 5532.
- 24. Zhang, Y.; Pei, S.; Wang, Y.; Cui, Z.; Li, N.; Zhu, Y.; Znang, H.; Jiang, Z. Dyes Pigm. 2013, 99, 1117.
- Kawatsuki, N.; Taniguchi, Y.; Kondo, M.; Haruyama, Y.; Matsui, S. *Macromolecules* 2015, 48, 2203.
- 26. Han, M.R.; Hara, M. New J. Chem. 2006, 30, 223.
- 27. Si, P.; Liu, J.; Deng, G.; Huang, H.; Xu, H.; Bo, S.; Qiu, L.; Zhen, Z.; Liu, X. RSC Adv. 2014, 4, 25532.
- 28. Li, Z.A.; Wu, W.; Ye, C.; Qin, J.; Li, Z. J. Phys. Chem. B. 2009, 113, 14943.
- Shevchenko, V.V.; Sidorenko, A.V.; Bliznyuk, V.N.; Tkachenko, I.M.; Shekera, O.V.; Smirnov N.N.; Maslyanitsyn, I.A.; Shigorin, V.D.; Yakimansky, A.V.; Tsukruk, V.V. Polymer 2013, 54, 6516.
- 30. Kosaka, N.; Oda, T.; Hiyama, T.; Nozaki, K. Macromolecules 2004, 37, 3159.
- 31. Peng, K.; Tomatsu, I.; Kros, A. Chem. Commun. 2010, 46, 4094.
- 32. Kong, B.; Cui, L.; Xie, P.; Zhang, R.; He, C.; Chung, N.T.S. Liq. Cryst. 2000, 27,16839.
- 33. Mizoshita, N.; Seki, T. Soft Matter 2006, 2,157.
- 34. Parmar, N.J.; Teraiya, S.B.; Patel, R.A.; Talpada, N.P. Tetrahedron Lett. 2011, 52, 2853.
- 35. Zhang, C.; Laine, R.M. J. Am. Chem. Soc. 2000, 122, 6979.
- Pakhomov AA, Kononevich YN, Stukalova MV, Svidchenko EA, Surin NM, Cherkaev G.V, Shchegolikhina, O.I.; Martynov, V.I.; Muzafarov, A.M. *Tetrahedron Lett.* 2016, *57*, 979.
- 37. Wu, W.; Wang, C.; Tang, R.; Fu, Y.; Ye, C.; Qin, J.; Li, Z. J. Mat. Chem. C. 2013, 1, 717.
- 38. Wu, W.; Ye, C.; Qin, J.; Li, Z. Chem. Asian J. 2013, 8, 1836.
- Rau, H. In: *Photochemistry and photophysics*; Rabek, J.K., Ed.; Boca Raton, FL: CRC Press, 1990;
 Vol. 2, p. 119.

- 40. Yager, K.G.; Barrett, C.J. J. Photochem. Photobiol. A Chem. 2006, 182, 250.
- 41. Zhang, Y.; Zhang, L.; Liu, H.; Sun, D.; Li. X. Cryst. Eng. Comm. 2015, 17, 1453.
- 42. Zhang, W.; Xie, J.; Shi, W.; Deng, X.; Cao, Z.; Shen, Q. Eur. Polym. J. 2008, 44, 872.
- 43. Lee, C.C.; Liu, M.C.; Kaneko, M.; Nakahira, K.; Takano, Y. Appl. Opt. 2005, 44, 6921.
- 44. Koshima, H.; Ojima, N.; Uchimoto, H. J. Am. Chem. Soc. 2009, 131, 6890.

Acceleration

Highlights

- \checkmark A synthetic route for a group of new azo dyes is described.
- \checkmark The design consists of using flexible alkyl chains and isolation groups.
- \checkmark The photoisomerization behavior of the obtained dyes was thoroughly investigated.
- \checkmark Prepared dyes have the potential to be used in stimuli responsive optical materials.

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Graphical Abstract

